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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM

Reference Method for the Continuous Measurement of Carbon Monoxide in the Atmosphere

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1. Good operating practices
2. Directions on how to assess data and qualify data
3. Directions on how to identify trouble and improve data quality
4. Directions to permit design of auditing activities
5. Procedures which can be used to select action options and relate them to costs

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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM

Reference Method for the Continuous Measurement of Carbon Monoxide in the Atmosphere

by

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PREFACE

Quality control is an integral part of any viable environmental monitoring activity. The primary goals of EPA's quality control program are to improve and document the credibility of environmental measurements. To achieve these goals, quality control is needed in nearly all segments of monitoring activities and should cover personnel, methods selection, equipment, and data handling procedures. The quality control program will consist of four major activities:

- Development and issuance of procedures
- Intra-laboratory quality control
- Inter-laboratory quality control
- Monitoring program evaluation and certification

All these activities are essential to a successful quality control program and will be planned and carried out simultaneously.

Accordingly, this first manual of a series of five has been prepared for the quality control of ambient air measurements. These guidelines for the quality control

of ambient carbon monoxide measurements have been produced under the direction the Quality Control Branch of the Quality Assurance and Environmental Monitoring Laboratory of NERC-RTP. The purpose of this document is to provide uniform guidance to all EPA monitoring activities in the collection, analysis, interpretation, presentation, and validation of quantitative data. In accordance with administrative directives to implement an Agency-wide quality control program, all EPA monitoring activities are requested to use these guidelines to establish intra-laboratory quality assurance programs in the conduct of all ambient air measurements of carbon monoxide. Your comments on the utility of these guidelines, along with documented requests for revision(s), are welcomed.

All questions concerning the use of this manual and other matters related to quality control of air pollution measurements should be directed to.

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During the months ahead, a series of manuals will be issued which describe guidelines to be followed during the course of sampling, analysis, and data handling. The use of these prescribed guidelines will provide a uniform approach in the various monitoring programs which allows the evaluation of the validity of data produced. The implementation of a total and meaningful quality control program cannot succeed without the full support of all monitoring programs. Your cooperation is appreciated.

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ABSTRACT

Guidelines for the quality control of ambient CO by the Federal reference method are presented. These include:

1. Good operating practices
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4. Directions to permit design of auditing activities
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The document is not a research report. It is designed for use by operating personnel.

This work was submitted in partial fulfillment of Contract Durham 68-02-0598 by Research Triangle Institute under the sponsorship of the Environmental Protection Agency. Work was completed as of May 1973.

1.0 INTRODUCTION

This document presents guidelines for implementing a quality assurance program for the continuous measurement of carbon monoxide in the atmosphere using non-dispersive infrared (NDIR) spectrometry.

The objectives of this quality assurance program for the NDIR method of measuring atmospheric carbon monoxide are to:

1) provide routine indication, for operating purposes, of unsatisfactory performance of personnel and/or equipment,
2) provide for prompt detection and correction of conditions which contribute to the collection of poor quality data, and
3) collect and supply information necessary to describe the quality of the data.

To accomplish the above objectives, a quality assurance program must contain the following components:

1) routine training and evaluation of operators,
2) routine monitoring of the variables and/or parameters which may have a significant effect on data quality,
3) development through auditing procedures, statements and evidence to qualify data and detect defects, and
4) action strategies to increase the level of precision in the reported data and/or to detect instrument defects or degradation and to correct same.

Implementation of a quality assurance program will result in data that are more uniform in terms of precision and accuracy. It will enable each monitoring network to continuously generate data that approach the highest level of accuracy attainable with the NDIR method.

This document is divided into three parts. They are:

Part I, Operations Manual - The operations manual sets forth recommended operating procedures, instructions for performing control checks designed to give an indication or warning that invalid or poor quality data are being collected, and instructions for performing certain special checks for auditing purposes.

Part II, Supervision Manual - The Supervision Manual contains brief directions for 1) the assessment of NDIR data, 2) collection of information to detect and/or identify trouble, 3) applying quality control procedures to improve data quality, and 4) varying the auditing or checking level to achieve a desired level of confidence in the validity of the outgoing data. Also, example monitoring strategies and costs as discussed in Part III are summarized in this manual.

Part III, Management Manual - The Management Manual presents procedures designed to assist in 1) detecting when data quality is inadequate, 2) assessing overall data quality, 3) determining the extent of independent auditing to be performed, 4) relating costs of data quality assurance procedures to a measure of data quality, and 5) selecting from the options available the alternative(s) which will enable one to meet the data quality goals by the most cost-effective means. Also, discussions on data presentation and personnel requirements are included in this manual.

The scope of this document has been purposely limited to that of a field document. Additional background information is contained in the final report under this contract.

PART I. OPERATIONS MANUAL

2.0 GENERAL

This operations manual sets forth recommended operating procedures for the continuous measurement of carbon monoxide in the atmosphere using non-dispersive infrared (NDIR) spectrometry. Quality control procedures and checks designed to give an indication or warning that invalid or poor quality data are being collected are written as part of the operating procedures, and are to be performed by the operator on a routine basis. In addition, the performance of special quality control procedures and/or checks as prescribed by the supervisor may be required of the operator on certain occasions.

The accuracy and/or validity of data obtained from this method depends upon instrument performance and the proficiency with which the operator performs his various tasks. Deviations from the recommended operational procedure may result in the collection of invalid data or at least reduce the quality of the data. The operator should make himself familiar with the manufacturer's operational instructions and with the rules and regulations concerning the NDIR method as written in the Federal Register, Vol. 36, No. 84, Part II, April 30, 1971 (see Appendix of this document).

For illustration purposes, directions throughout this document are written in terms of a 24-hour sampling period (i.e., 24 hours between zero and span calibrations), and an auditing or checking level of 7 checks out of a lot size of 100 sampling periods. Sampling period durations and auditing levels are subject to change by the supervisor and/or manager. Such change would not alter the basic directions for performing the operation. Also, certain control limits as given in this manual represent best estimates for use in the beginning of a quality assurance program and are, therefore, subject to change as field data are collected.

It is assumed that an analyzer which meets reference method specifications has been set up and checked out according to the manufacturer's directions by an experienced technician.

2.1 Operating Procedures

The sequence of operations to be performed during each sampling period is given in Figure 1. Each operation or step in the process is identified by a block. Quality checkpoints in the measurement process, for which appropriate quality control limits are assigned, are represented by blocks enclosed by heavy lines. Other checkpoints involve go/no-go checks and/or subjective judgments by the operator with proper guidelines for decision making spelled out in the procedures. *These operations and checks are discussed sequentially as one progresses step by step through the sequence of actions in Figure 1.*

The operator is also responsible for maintaining certain records. Specifically the following log books are maintained on site:

1) Operational Data Log Book. Completed daily check sheets (see Figure 5) are filed in the operational data log book. Also, special quality control checks are recorded on the form in Figure 6 and stored in this log book.

2) Calibration Log Book. Completed calibration conversion sheets (see Figure 4), calibration curves (see Figure 3), and calibration schedules are filed in the calibration log book.

3) Maintenance Log Book. Maintenance records and schedules make up the maintenance log book. Schedules should be made up from manufacturer's recommendations and altered as detailed experience suggests.

A typical monitoring setup consisting of a sample introduction system, analyzer system, and data recording and display system is illustrated in Figure 2.

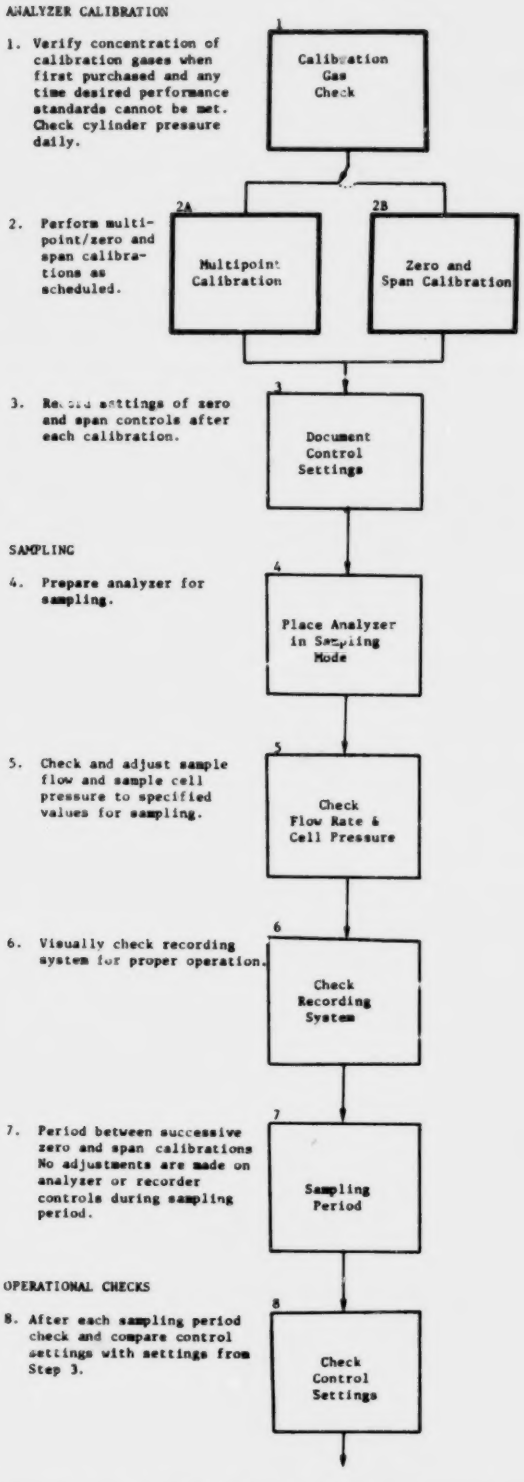
ANALYZER CALIBRATION
1. Verify concentration of calibration gases when first purchased and any time desired performance standards cannot be met. Check cylinder pressure daily.
1
Calibration Gas Check
2. Perform multi-point/zero and span calibrations as scheduled.
2A
Multipoint Calibration
2B
Zero and Span Calibration
3. Record settings of zero and span controls after each calibration.
3
Document Control Settings
SAMPLING
4. Prepare analyzer for sampling.
4
Place Analyzer in Sampling Mode
5. Check and adjust sample flow and sample cell pressure to specified values for sampling.
5
Check Flow Rate & Cell Pressure
6. Visually check recording system for proper operation.
6
Check Recording System
7. Period between successive zero and span calibrations No adjustments are made on analyzer or recorder controls during sampling period.
7
Sampling Period
OPERATIONAL CHECKS
8. After each sampling period check and compare control settings with settings from Step 3.
8
Check Control Settings

Figure 1: Operational Flow Chart of the Measuring Process

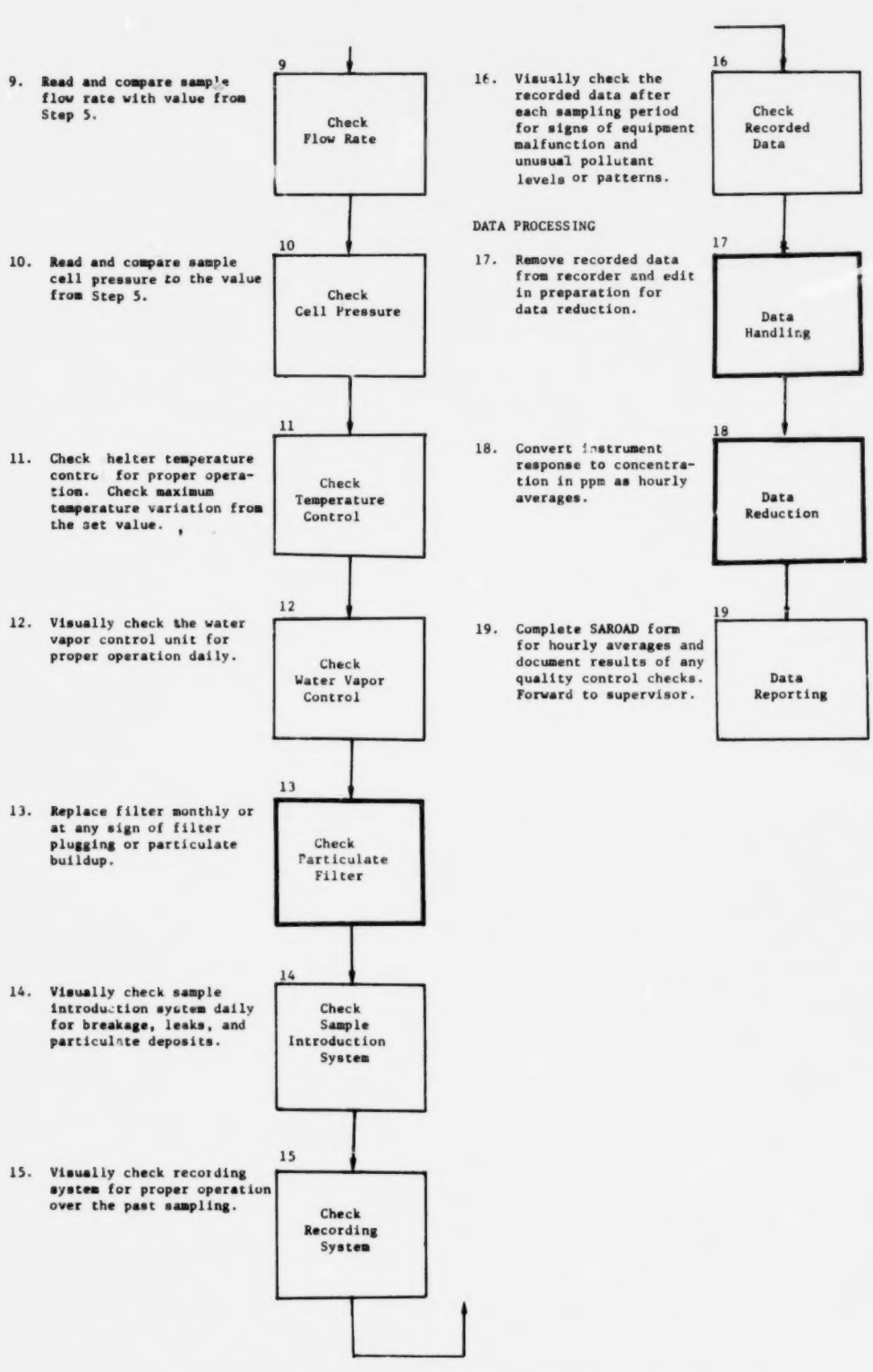
9. Read and compare sample flow rate with value from Step 5.
9
Check Flow Rate
10. Read and compare sample cell pressure to the value from Step 5.
10
Check Cell Pressure
11. Check heater temperature control for proper operation. Check maximum temperature variation from the set value.
11
Check Temperature Control
12. Visually check the water vapor control unit for proper operation daily.
12
Check Water Vapor Control
13. Replace filter monthly or at any sign of filter plugging or particulate buildup.
13
Check Particulate Filter
14. Visually check sample introduction system daily for breakage, leaks, and particulate deposits.
14
Check Sample Introduction System
15. Visually check recording system for proper operation over the past sampling.
15
Check Recording System
16. Visually check the recorded data after each sampling period for signs of equipment malfunction and unusual pollutant levels or patterns.
16
Check Recorded Data
DATA PROCESSING
17. Remove recorded data from recorder and edit in preparation for data reduction.
17
Data Handling
18. Convert instrument response to concentration in ppm as hourly averages.
18
Data Reduction
19. Complete SAROAD form for hourly averages and document results of any quality control checks. Forward to supervisor.
19
Data Reporting

Figure 1: Operational Flow Chart of the Measuring Process (cont'd)

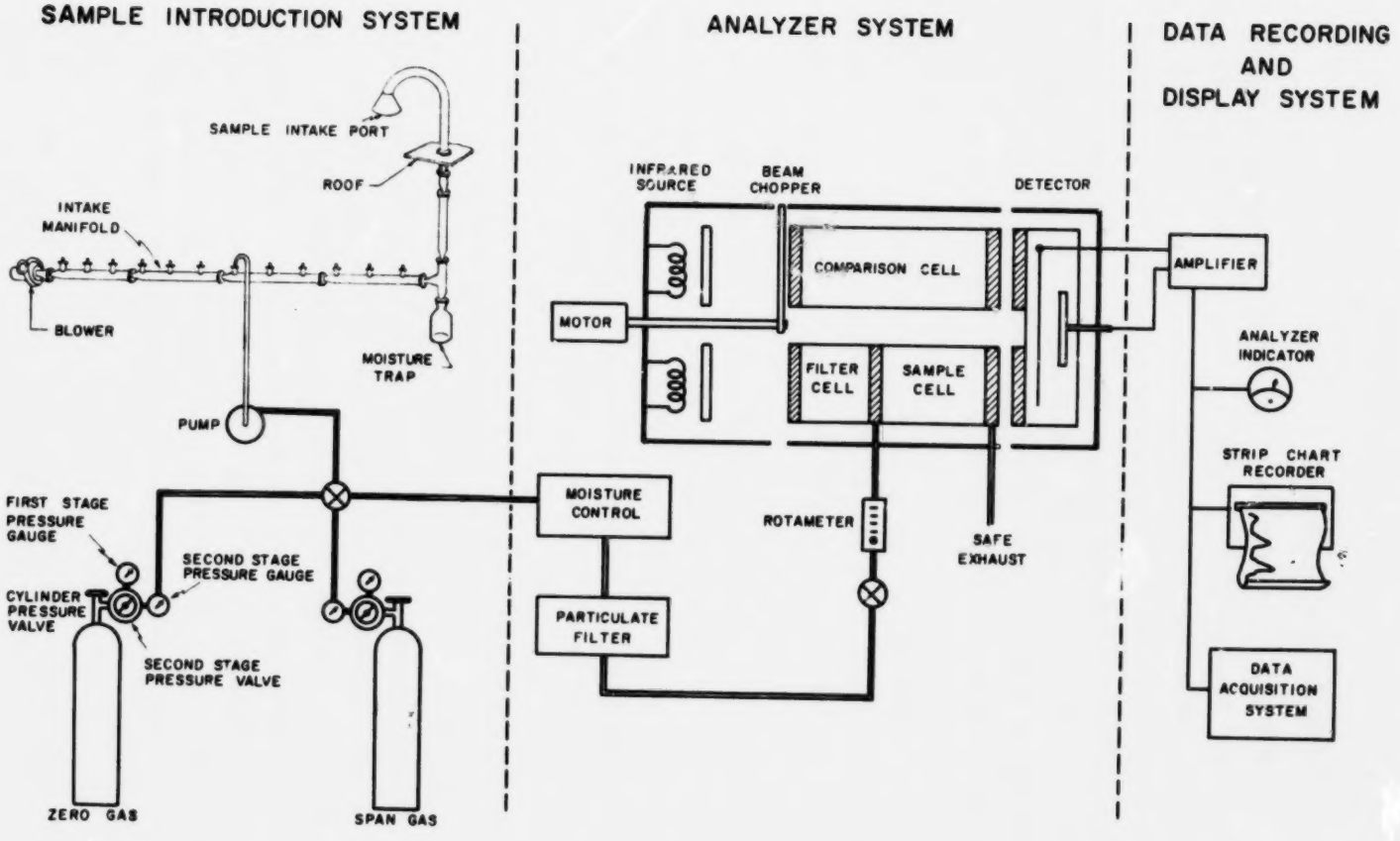

Figure 2: Carbon Monoxide Monitoring System Flow Chart

ANALYZER CALIBRATION

Step 1. Calibration Gas Check

A multipoint calibration requires calibration gases with concentrations corresponding to approximately 10, 20, 40, and 80 percent of full scale and a zero gas containing less than 0.1 mg CO/m^3. It is further recommended that calibration gases certified to be within $\pm$ 2 percent of the stated value be purchased in high pressure cylinders with inside surfaces of a chromium-molybdenum alloy of low iron content or other appropriate linings. Store the cylinders in areas not subject to extreme temperature changes (e.g., do not expose to direct sunlight). It is recommended that CO in synthetic air be used for all calibration gases.

It is recommended that at least three (3) control gas samples, assayed and certified to be within $\pm$ 1 percent of the stated level of CO, be obtained for use in the auditing process for assessing data quality. (Sections 2.2, 3.1, and 4.1 discuss the auditing process.) The CO concentration of the control samples should be distributed to cover the range of about 5 to 40 ppm.* These auditing gases (control samples) could be purchased in size 3 cylinders to allow for portability and to insure that the sample is exhausted before the CO concentration has changed significantly due to deterioration with time.

A. Concentration Verification

When a quality assurance program is first started, the concentration of all calibration gases on hand should be verified. Two verification procedures are discussed herein. The first method represents the minimum action necessary to verify concentration values. It is possible that the certified concentration values of calibration gases and auditing gases obtained from the same supplier may be equally in error and, consequently, be accepted as good by this method. A second and somewhat more thorough procedure which eliminates this possibility is given using gases from different sources.

---

*The factor for converting CO from volume (ppm) to mass (mg/m^3) units is: 1 ppm = 1.145 mg/m^3 at 25°C and 760 mmHg.

Once the calibration gases have been initially verified, new gases can be verified at the time of purhcase in a routine fashion by measuring against the old gases.

1. Method I

   a) Set up and check out the analyzer.

   b) Calibrate the analyzer with the auditing gases (see Step 2A, page 11 for calibration procedures).

   c) Construct a calibration curve from at least four (4) points, i.e., zero, span, and two (2) upscale points (see Step 2A, Procedure 24 on page 14 for guidance in constructing a calibration curve).

   d) Check the calibration curve and if any of the measured points deviate from the smooth curve by more than $\pm$ (1.0 + 0.01 C_a)*ppm, have that cylinder of auditing gas reanalyzed. In some cases a subjective decision will have to be made by the supervisor as to whether it is the span gas or one of the upscale gases that is in error. If all measured points are within the above limits, use the best fit curve as the correct calibration curve.

   e) Measure the calibration gases.

   f) Have all calibration gases whose measured value differs from its certified value by more than $\pm$ (1.0 + 0.02 C_c)**ppm reanalyzed until an acceptable set of calibration gases is obtained.

   g) Obtain and verify new calibration gases before old ones are exhausted by calibrating the analyzer with the old calibration gas. Accept the new gas as good if the measured and certified values are within $\pm$ (1.0 + 0.02 C_c)ppm of each other; reject the gas otherwise.

---

*1.0 ppm is based on the 3σ value for repeatibility from a collaborative test (Ref. 1), 0.01 is the stated accuracy of the auditing gas, and C_a is the certified concentration of the auditing gas.

**0.02 is the stated accuracy of the calibration gas, and C_c is the certified concentration of the calibration gas.

2. Method II

a) Set up and check out the analyzer.

b) Have two (2) sets of calibration gases ($\pm$ 2%) from different suppliers available.

c) Have one set of auditing gases ($\pm$ 1%) from another supplier if possible; or when available, "standard gases" of EPA's recommendation.

d) Calibrate the analyzer with the auditing or standard gases (see Step 2A, page 11 for calibration procedure).

e) Construct a calibration curve from at least four (4) points, i.e., zero, span and two (2) upscale points (see Step 2A, Procedure 24 on page 14 for guidance in constructing a calibration curve).

f) Check the calibration curve and if either one of the two upscale points deviates more than $\pm$ (1.0 + 0.01 C_a)ppm from the smooth calibration curve, have that cylinder of auditing gas reanalyzed. In some cases a subjective decision will have to be made by the supervisor as to whether it is the span gas or one of the two upscale gases that is in error. If both upscale points are within the above limits, use the best fit curve as the correct calibration curve.

g) Measure both sets of calibration gases.

h) If both sets of calibration gases disagree (i.e., measured and certified values differ by more than $\pm$ (1.0 + 0.02 C_c)ppm for cylinders of each set), have all calibration and auditing gases reanalyzed.

i) If one set of calibration gases agrees (i.e., measured and certified values agree within $\pm$ (1.0 + 0.02 C_c)ppm for each cylinder), accept that set as good and have the other set reanalyzed. If both sets agree, accept both sets as good.

j) Obtain and verify new calibration gases before the old gases are exhausted by calibrating the analyzer with the old gases and measuring the new calibration gas. Accept the new gas as good if the measured and certified values are within $\pm$ (1.0 + 0.02 C_c)ppm of each other; reject the gas otherwise.

B. Cylinder Pressure Check

Before each calibration, check the cylinder pressure of each calibration gas to be used. Order replacement for any cylinder with less than 2.1×10^6 Nm^{-2} (300 psi) pressure.

Step 2A. Multipoint Calibration

A. Frequency of Calibration

A multipoint calibration is required when:

1) the analyzer is first purchased,
2) the analyzer has had maintenance which could affect its response characteristics, or
3) when results from the auditing process show that the desired performance standards are not being met (see A of Section 2.2).

B. Calibration Procedures

Follow the manufacturer's detailed instructions when calibrating a specific analyzer. General procedures are:

1) Turn the power on and let the analyzer warm up by sampling ambient air. This usually requires several hours (as many as 24 to 48 hours) depending on the individual analyzer.
2) Connect zero gas to the analyzer.
3) Open the gas cylinder pressure valve (see Figure 2, page 7). Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 3.4×10^4 Nm^{-2} (5 psi) more than the desired sample cell pressure. Caution: Do not exceed the pressure limit of the sample cell.

4) Set the sample flow rate as read by the rotameter (read the widest part of the float) to the value that is to be used during sampling.

5) Let the zero gas flow long enough to establish a stable trace. Allow at least 5 minutes for the analyzer to stabilize.

6) Adjust the zero control knob until the trace corresponds to the line representing 5 percent of the strip chart width above the chart zero or baseline. The above is to allow for possible negative zero drift. If the strip chart already has an elevated baseline, use it as the zero setting.

7) Let the zero gas flow long enough to establish a stable trace. Allow at least 5 minutes for this. Mark the strip chart trace as adjusted zero.

8) Disconnect the zero gas.

9) Connect the span gas with a concentration corresponding to approximately 80 percent full scale.

10) Open the gas cylinder pressure valve (see Figure 2, page 7). Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 3.4×10^4 Nm^{-2} (5 psi) more than the desired sample cell pressure.

11) Set the sample flow rate, as read by the rotameter, to the value that is to be used during sampling.

12) Let the span gas flow until the analyzer stabilizes.

13) Adjust the span control until the deflection corresponds to the correct percentage of chart as computed by

$$\frac{C_S(ppm)}{C_f(ppm)} \times 100 + 5\ (\%\ \text{zero offset}) = \text{correct percentage of chart}$$

where

C_S = concentration of span gas in ppm,

and

C_f = full scale reading of analyzer in ppm.

As an example see Figure 3, page 15, where the % zero offset is 5 and the correct percentage of chart for the span gas of 40 ppm would be

$$\frac{40 \text{ ppm}}{50 \text{ ppm}} \times 100 + 5 = 85.$$

14) Allow the span gas to flow until a stable trace is observed. Allow at least 5 minutes. Mark the strip chart trace as adjusted span and give concentration of span gas in ppm.

15) Disconnect the span gas.

16) Repeat Procedures 2 through 8 and
   a) if no readjustment is required, go to Procedure 17;
   b) if a readjustment greater than 1 ppm is required, repeat Procedures 9 through 16.

17) Lock the zero and span controls.

18) Connect the calibration gas with a concentration corresponding to approximately 10 percent full scale to the analyzer.

19) Open the gas cylinder pressure valve (see Figure 2, page 7). Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 3.4×10^4 Nm^{-2} (5 psi) more than the desired sample cell pressure.

20) Set the sample flow rate to the value used during sampling.

21) Let the calibration gas flow until the strip chart trace stabilizes. Note: No adjustments are made at this point.

22) Disconnect the calibration gas.

23) Repeat Procedures 18 through 22 for each of the calibration gases with concentrations corresponding to approximately 20 and 40 percent of full scale in that order.

24) Fill in the information required on a calibration sheet and construct a calibration curve of deflection as percent of chart versus concentration in ppm as illustrated in Figure 3. Draw a best fit, smooth curve passing through the zero and span points and minimizing the deviation of the three remaining upscale points from the curve. The calibration curve should have no inflection points, i.e., it should either be a straight line or bowed in one direction only. Curve fitting techniques may be used in constructing the calibration curve by applying appropriate constraints to force the curve through the zero and span points. This procedure becomes quite involved, however; and the most frequently used technique is to fit the curve by eye.

25) Recheck any calibration point deviating more than $\pm$ (1.0 + 0.02 C_c)ppm from the smooth calibration curve. If the recheck gives the same results, have that calibration gas reanalyzed. Use the best fit curve as the calibration curve.

26) Fill in the calibration conversion sheet (see Figure 4, page 16) from the calibration curve.

27) In certain situations the supervisor may request that the calibration be repeated (replicated). In this case obtain both sets of data and follow his instructions for preparing a calibration curve.

Step 2B. Zero and Span Calibration

A. Frequency of Zero and Span Calibration

A zero and span calibration is performed before and after each sampling period (taken as every 24 hours here) or as directed by the supervisor.

Location_____Date_____Operator_____

Analyzer No._____Range_____Flow Rate_____Cell Pressure _____

Zero Gas_____ Cylinder Pressure_____Cylinder No._____

Upscale gas (80%)_____ Cylinder Pressure_____Cylinder No._____
(10%)_____ Cylinder Pressure_____Cylinder No._____
(20%)_____ Cylinder Pressure_____Cylinder No._____
(40%)_____ Cylinder Pressure_____Cylinder No._____

Zero Control Setting_____Span Control Setting_____

Recorder Type _____Serial No. _____

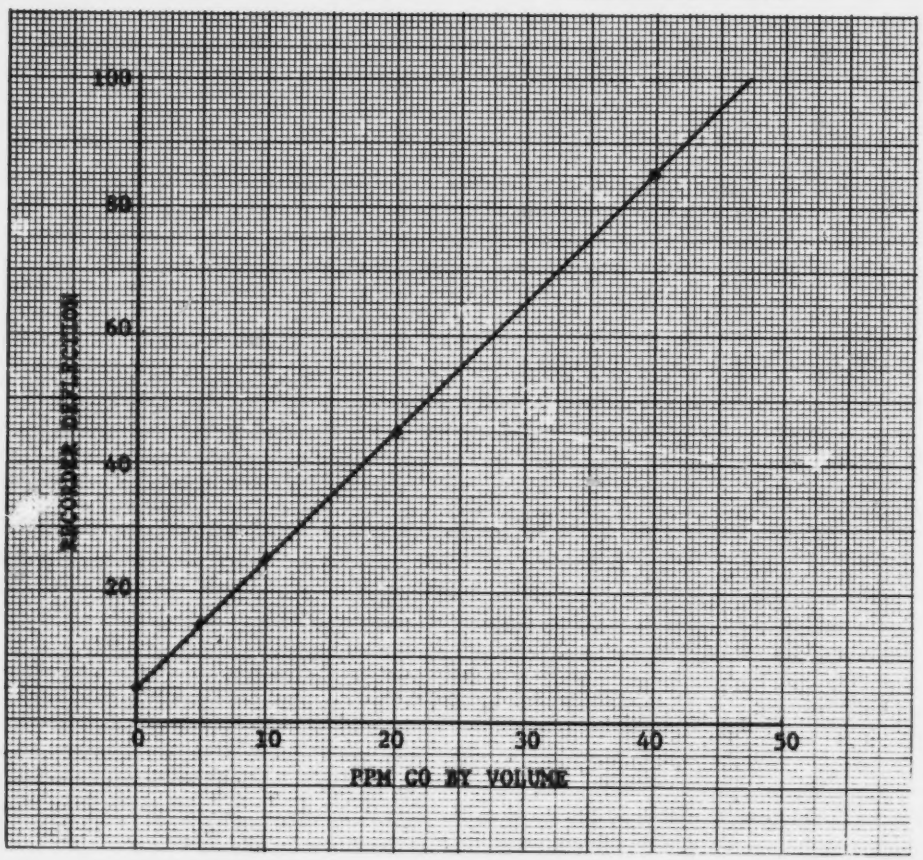

Figure 3: Sample Calibration Curve

Analyzer No. _____ Date of Calibration_____

% Chart	PPM	% Chart	PPM	% Chart	PPM	% Chart	PPM	% Chart	PPM
0.0		20.5		40.5		60.5		80.5	
0.5		21.0		41.0		61.0		81.0	
1.0		21.5		41.5		61.5		81.5	
1.5		22.0		42.0		62.0		82.0	
2.0		22.5		42.5		62.5		82.5	
2.5		23.0		43.0		63.0		83.0	
3.0		23.5		43.5		63.5		83.5	
3.5		24.0		44.0		64.0		84.0	
4.0		24.5		44.5		64.5		84.5	
4.5		25.0		45.0		65.0		85.0	
5.0									
5.5		25.5		45.4		65.5		85.5	
6.0		26.0		46.0		66.0		86.0	
6.5		26.5		46.5		66.5		86.5	
7.0		27.0		47.0		67.0		87.0	
7.5		27.5		47.5		67.5		87.5	
8.0		28.0		48.0		68.0		88.0	
8.5		28.5		48.5		68.5		88.5	
9.0		29.0		49.0		69.0		89.0	
9.5		29.5		49.5		69.5		89.5	
10.0		30.0		50.0		70.0		90.0	
10.5		30.5		50.5		70.5		90.5	
11.0		31.0		51.0		71.0		91.0	
11.5		31 5		51.5		71.5		91.5	
12.0		32.0		52.0		72.0		92.0	
12.5		32.5		52.5		72.5		92.5	
13.0		33.0		53.0		73.0		93.0	
13.5		33.5		53.5		73.5		93.5	
14.0		34.0		54.0		74.0		94.0	
14.5		34.5		54.5		74.5		94.5	
15.0		35.0		55.0		75.0		95.0	
15.5		35.5		55.5		75.5		95.5	
16.0		36.0		56.0		76.0		96.0	
16.5		36.5		56.5		76.5		96.5	
17.0		37.0		57.0		77.0		97.0	
17.5		37.5		57.5		77.5		97.5	
18.0		38.0		58.0		78.0		98.0	
18.5		38.5		58.5		78.5		98.5	
19.0		39.0		59.0		79.0		99.0	
19.5		39.5		59.5		79.5		99.5	
20.0		40.0		60.0		80.0		100.0	

Figure 4: Table for Converting Trace Deflection in Percent of Chart to Concentration in PPM

Analyzer No. _____ Date of Calibration _____

% Chart	PPM	% Chart	PPM	% Chart	PPM	% Chart	PPM	% Chart	PPM
0.0		20.5		40.5		60.5		80.5	
0.5		21.0		41.0		61.0		81.0	
1.0		21.5		41.5		61.5		81.5	
1.5		22.0		42.0		62.0		82.0	
2.0		22.5		42.5		62.5		82.5	
2.5		23.0		43.0		63.0		83.0	
3.0		23.5		43.5		63.5		83.5	
3.5		24.0		44.0		64.0		84.0	
4.0		24.5		44.5		64.5		84.5	
4.5		25.0		45.0		65.0		85.0	
5.0									
5.5		25.5		45.4		65.5		85.5	
6.0		26.0		46.0		66.0		86.0	
6.5		26.5		46.5		66.5		86.5	
7.0		27.0		47.0		67.0		87.0	
7.5		27.5		47.5		67.5		87.5	
8.0		28.0		48.0		68.0		88.0	
8.5		28.5		48.5		68.5		88.5	
9.0		29.0		49.0		69.0		89.0	
9.5		29.5		49.5		69.5		89.5	
10.0		30.0		50.0		70.0		90.0	
10.5		30.5		50.5		70.5		90.5	
11.0		31.0		51.0		71.0		91.0	
11.5		31.5		51.5		71.5		91.5	
12.0		32.0		52.0		72.0		92.0	
12.5		32.		52.5		72.5		92.5	
13.0		33.0		53.0		73.0		93.0	
13.5		33.5		53.5		73.5		93.5	
14.0		34.0		54.0		74.0		94.0	
14.5		34.5		54.5		74.5		94.5	
15.0		35.0		55.0		75.0		95.0	
15.5		35.5		55.5		75.5		95.5	
16.0		36.0		56.0		76.0		96.0	
16.5		36.5		56.5		76.5		96.5	
17.0		37.0		57.0		77.0		97.0	
17.5		37.5		57.5		77.5		97.5	
18.0		38.0		58.0		78.0		98.0	
18.5		38.5		58.5		78.5		98.5	
19.0		39.0		59.0		79.0		99.0	
19.5		39.5		59.5		79.5		99.5	
20.0		40.0		60.0		80.0		100.0	

Figure 4: Table for Converting Trace Deflection in Percent of Chart to Concentration in PPM

B. Zero and Span Calibration Procedures

1) Connect the span gas with a concentration value corresponding to 80 percent of full scale, or other values as directed by the supervisor, to the analyzer.
2) Open the gas cylinder pressure valve and adjust the secondary pressure valve (see Figure 2, page 7) until the secondary pressure gauge reads approximately 3.4×10^4 Nm^{-2} (5 psi) more than the desired sample cell pressure.
3) Set the sample flow rate as read by the rotameter (read the widest part of the float) to the value to be used when sampling.
4) Let the span gas flow long enough to establish a stable trace on the strip chart recorder; allow at least 5 minutes. Mark the chart trace as an unadjusted span. Record unadjusted span reading in ppm on form in Figure 5, page 18, under column entitled "Unadjusted Calibration."
5) Disconnect the span gas.
6) Connect zero gas to the analyzer.
7) Open the gas cylinder pressure valve and adjust the secondary pressure valve until the secondary pressure gauge reads approximately 3.4×10^4 Nm^{-2} (5 psi) more than the desired sample cell pressure.
8) Set the sample flow rate as read by the rotameter to the value that is used when sampling.
9) Let the zero gas flow long enough to establish a stable zero trace on the strip chart recorder; allow at least 5 minutes. Mark the chart trace as an unadjusted zero. Record the unadjusted zero reading in ppm on form in Figure 5, page 18 under column titled "Unadjusted Calibration." A supervisor could use this data to compute a mean and standard deviation in ppm for zero drift using unadjusted calibration data from at least 25 sampling periods (see Section 4.1 for computing standard deviations).

CO ANALYZER DAILY CHECK SHEET

Station Name _____ Location _____

Analyzer Number _____

Date	Operator	Sample Flow Rate (ℓ/min)		Sample Cell Pressure (Nm^{-2})		Cylinder Pressure (Nm^{-2})		New Control Knob Setting		Unadjusted Calibration	
		Initial	Final	Initial	Final	Zero	Span	Zero	Span	Zero	Span

Figure 5: Sample Daily Check Sheet

If the unadjusted zero trace is more than $\pm$ 3σ ppm from the true zero value, check the temperature control for the analyzer and/or shelter for proper operation and other likely causes. Report the situation to the supervisor. Continue with the calibration.

10) Adjust the zero control knob until the trace corresponds to the true zero setting. Let the zero gas flow until a stable trace is obtained. Mark the chart trace as an adjusted zero.

11) Disconnect the zero gas.

12) Reconnect the span gas and let flow until analyzer has stabilized; then adjust the span control until the deflection on the strip chart corresponds to the span gas concentration in ppm using the calibration conversion table as illustrated in Figure 4, page 16. Let the strip chart trace stabilize. Mark the chart trace as an adjusted span with the span gas concentration in ppm. A supervisor could compute a mean and standard deviation in ppm for span drift using data from at least 25 sampling periods (obtain span drift in ppm by subtracting the true span gas concentration from the unadjusted span reading as recorded in the last column of the form in Figure 5). If the required adjustment is more than $\pm$ 3σ ppm, try to determine the cause and report the situation to the supervisor. Continue with the calibration.

13) Disconnect the span gas.

14) If a span adjustment greater than $\pm$ 1.0 ppm (2% of chart) is required, repeat Procedures 6 through 12 until no adjustments are required.

15) Lock the zero and span controls.

Step 3. Record Analyzer Control Settings

Record the following information on the check sheet (see Figure 5, page 18). Record 1 and 2 under "New Control Knob Settings," and 3 and 4 under "Cylinder Pressure." Include units of pressure if other than newtons per square meter (Nm^{-2}) are used.

1) Zero control knob position,
2) Span control knob position,
3) Zero gas cylinder pressure (read first stage pressure gauge),
4) Span gas cylinder pressure (read first stage pressure gauge).

SAMPLING

Step 4. Place Analyzer in Sampling Mode

Connect analyzer to sample introduction system. Allow time for the analyzer to stabilize.

Step 5. Sample Flow and Sample Cell Pressure Check

Check and, if necessary, adjust the sample flow to the desired value.

Record the sample flow (include units if other than ℓ/min) and sample cell pressure on the daily check sheet as "Initial" value (see Figure 5, page 18).

Step 6. Recording System Check

Check the strip chart recorder for proper operation including:

1) chart speed control setting,
2) gain control setting,
3) ink trace for readability,
4) signs of excess noise, and
5) the recorder's deadband (according to manufacturer's directions about once a month).

Automatic data acquisition systems incorporating magnetic tape recorder or punched paper tape are checked for proper operation according to the manufacturer's instructions.

Step 7. Sampling Period

The sampling period is defined as the time interval between successive zero and span calibrations (usually 24 hours).

Do not change control settings on the analyzer or recording system during the sampling period.

OPERATIONAL CHECKS

Step 8. Zero and Span Control Settings

Compare the zero and span control settings to the values recorded on the check sheet (Figure 5) under "New Control Knob Settings."

If the settings before and after the sampling period do not agree, note the difference in the data log book and

1) perform the normal zero and span calibration. If the required zero and/or span correction is less than $\pm$ 1.0 ppm, continue in the usual manner (this assumes that the original settings were recorded wrong or that the change in setting was not large),
2) if the required zero and/or drift correction is greater than $\pm$ 1.0 ppm, mark the data void and report the situation to the supervisor. Continue normal operations.

Step 9. Sample Flow Rate

Read the sample flow rate from the rotameter. Record flow rate (ℓ/min) on daily check sheet (Figure 5) as "Final" value. Compare initial and final readings.

If the change is greater than $\pm$ 20 percent of the initial value, check the particulate filter for plugging (see Step 13) and the sample air pump system for proper operation. Take corrective action.

Compute percent difference by

$$\frac{Q_i - Q_f}{Q_i} \times 100 = \text{percent}$$

where

Q_i = initial flow rate (ℓ/min)

and

Q_f = final flow rate (ℓ/min).

Step 10. Sample Cell Pressure

Check the sample cell pressure and compare with the initial pressure recorded on the daily check sheet (Figure 5, page 18). If the pressure varied during the sampling period and

$$\frac{\text{final pressure}}{\text{initial pressure}} \times 100 \leq 10\% ,$$

try to determine the cause and initiate corrective action. Report the change to the supervisor and record the magnitude and direction of change on the quality control check sheet (Figure 6, page 23) under "Data Quality Statement."

If the pressure varied by more than 10%, the supervisor should void the data and locate and correct the cause before sampling is resumed.

Step 11. Temperature Control Check

Each shelter should be equipped with a temperature-indicating device such as a wall thermometer or a maximum and minimum registering thermometer. Check the thermometer to verify that the temperature control system is operating within limits. Control limits on allowable temperature variations are determined by a supervisor from the temperature variation sensitivity check in Section 2.3 and in conjunction with desired accuracy. If a larger than usual or allowable temperature variation is observed, record cause and corrective action in the maintenance log book

QUALITY CONTROL CHECKS

City_____ Pollutant_____

Site Location_____ Analyzer Number_____

Site Number_____ Date_____

Supervisor Responsible for Checks (Signature) _____

Auditing Level n checks / N sampling periods	Type of Quality Control Check	Result of Check	Corrective Action Taken	Operator Performing Check

Data Quality Statement:

Figure 6: Sample Form for Reporting Results of Quality Control Checks

maintained in the shelter. If no cause is identified, or if the cause is determined but cannot be corrected immediately, report it to the supervisor. Reset the maximum and minimum registering thermometer after checking temperature variation for a sampling period.

Step 12. Water Vapor Control Check

Several techniques may be used to control water vapor interference. Refrigeration and drying agents are two of the most commonly used methods. Daily checks for these two methods are:

1) Drying Agents - The color of the drying agent (i.e., silica gel or other indicating dessicants) is checked daily and replaced or rejuvinated when necessary as indicated by a change in color.
2) Refrigeration - Check the moisture trap between the refrigerator unit and the analyzer for condensed moisture. Any sign of moisture indicates a malfunction in the control unit. Check the compressor for proper operation by measuring the temperature of the cooling coil (units are designed to operate at a specified temperature). Drain condensate from the cold trap after each sampling period and before each calibration (or leave the drain cock open during sampling). Report any period(s) of time that the sample air dewpoint was lower than the refrigerator dewpoint.

Take corrective action and/or notify the supervisor at any sign of malfunction or inadequacy of the water vapor control unit. Report with the data, by recording on the strip chart record, any period of time for which the moisture control unit was not operating or its effectiveness was not certain.

Document malfunctions and corrective actions in the maintenance log book.

Step 13. Particulate Filter Check

A filter with a porosity of 2 to 10 micrometers is used to keep large particles from reaching the sample cell.

With no filter in the system observe the sample flow rate. Place a clean filter in the filter holder and read the new flow rate. Any drop in flow rate is due to the clean filter. Record the magnitude of the drop in the maintenance log book.

Initially measure the flow rate with and without the "dirty" filter once a month. Replace the filter if the flow rate drop for the dirty filter divided by the drop caused by the clean filter is more than 2. Experience will suggest how often such checks need to be made for a given site.

Step 14. Sample Introduction System Check

A sample introduction system usually consists of an intake port, trap for moisture and large particulates, horizontal sampling manifold, and exhaust blower as illustrated in Figure 2, page 7.

Check the moisture trap for accumulated water and large particles. Remove, clean, and replace the trap if any moisture and/or particulates are present.

Visually check the sample introduction system for breakage, leaks, foreign objects in the intake port (e.g., spider webs, wasp nests), and deposited particulates or excess moisture in the horizontal sampling manifold.

The above checks are made each sampling period (usually daily). Conditions such as a break in the manifold or a leaky joint in the sampling manifold network which could affect data quality are reported with the data by a brief description of the condition under "Data Quality Statements" on the form in Figure 6, page 23, and by marking the strip chart trace as void and reporting the situation to the supervisor. Take corrective action and document in maintenance log book.

Step 15. Recording System Check and Servicing

Check the recording system for signs of recorder malfunctions occurring during the past sampling period. Specific procedures for checking and servicing will depend on the type of recording system used.

Check and service automatic data acquisition systems according to the manufacturer's instructions.

For a strip chart recorder check to see that:

1) the recorder did not run out of chart paper,
2) there is a continuous inked narrow trace for the entire sampling period, and
3) there was a uniform advancement of the chart paper by checking the start and end times on the chart and comparing with actual start and end times.

Malfunctions in the recording system resulting in loss or invalidation of data are corrected and documented in the maintenance log book. The sampling interval affected by the malfunction is identified on the strip chart record for that sampling period.

Service the recorder for the next sampling period:

1) Check the ink supply and refill if less than 1/4 full.
2) Install a new roll of chart paper as necessary.

Step 16. Visual Check of Recorded Data

Check and edit the strip chart record for the past sampling period to detect signs of monitoring system malfunctions and to validate the data.

Typical points to look for which may indicate system problems are:

1) A straight trace for several hours (other than minimum detectable).
2) Excess noise as indicated by a wide solid trace, or erratic behavior such as spikes that are sharper than is possible with the normal instrument response time. Noisy outputs usually result when analyzers are exposed to vibration sources.
3) A long steady increase or decrease in deflection.

4) A cyclic pattern of the trace with a definite time period indicating a sensitivity to changes in temperature or parameters other than CO concentration.

5) Periods where the trace drops below the zero baseline. This may result from a larger-than-normal drop in the ambient room temperature or power line voltage.

If any of the above conditions are detected, data should be flagged, troubleshooting done, and the supervisor informed. Data should be declared invalid only if malfunction of the instrument is detected; otherwise, it should be reported.

Also, for data validation, a graph could be prepared by the supervisor from previous data (e.g., 1 year of data) containing the average and $\pm 3\sigma$ values for the hourly averages for reference when editing data. Figure 7, page 28, is an illustration of such a graph. The occurrence of any one or more of the conditions listed below should be investigated for possible causes (e.g., extra heavy traffic, shift in peak traffic hours, or periods of atmospheric stagnation with high pollution levels):

1) an estimated 1 hour average falls outside the $\pm 3\sigma$ limits for that specific hour,

2) the daily pattern has shifted to left or right by 2 or more hours, and

3) abnormal pattern such as no peaks.

Document any causes known or suspected or the absence of any known causes on the form in Figure 6, page 23, under "Data Quality Statement."

DATA PROCESSING

Step 17. Data Handling

At the end of each sampling period the operator should make certain that the strip chart contains the following information:

1) Sampling station number, location, pollutant being measured, and operator.

2) Starting time and date. Ending time and date.

3) Proper identification of unadjusted zero and adjusted zero traces.

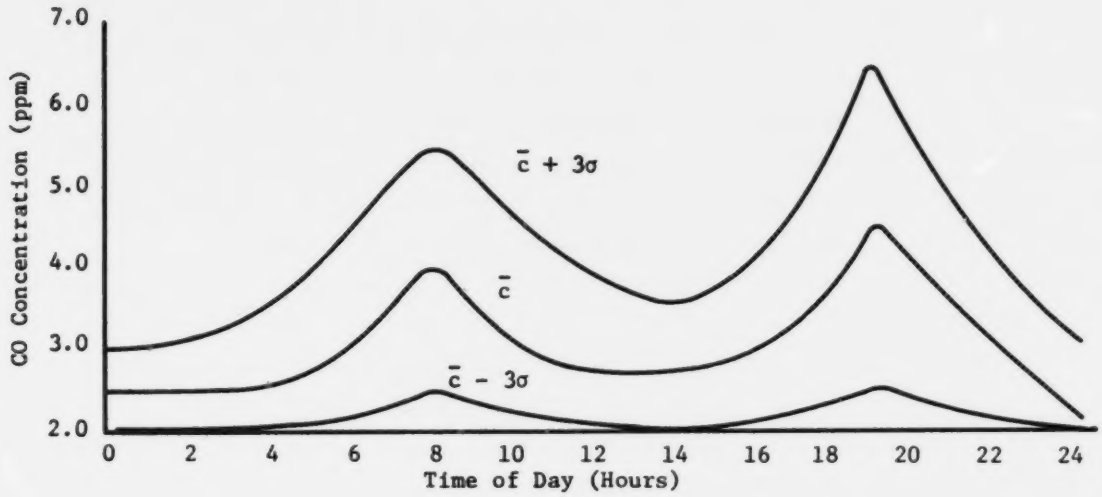

Figure 7: A Sample Graph of the Mean ($\bar{c}$) and 3σ Limits of Hourly CO Concentrations for a 24-Hour Period

4) Proper identification of unadjusted and adjusted span traces, and the concentration in ppm of the span gas.
5) Editing information identifying any periods of invalid data due to equipment failure or other known causes.

Step 18. Data Reduction

A. Procedure for Reading Hourly Averages from Strip Chart Records

To determine the hourly average concentration from a strip chart record, the following procedures are used:

1) Obtain the strip chart record for the sampling period in question. The record must have adjusted span and zero traces at the beginning of the sampling period and unadjusted span and zero traces at the end of the sampling period.
2) Fill in the identification data called for at the top of an hourly averages sheet (see Figure 8, page 29).

CITY_____ SITE NUMBER_____

SITE LOCATION_____ POLLUTANT_____

DATE_____ OPERATOR_____

CHECKER_____

Hour	Reading		Zero Baseline		Difference		Add +5		PPM	
	Original	Check	Original	Check	Original	Check	Original	Check	Original	Check
0-1										
1-2										
2-3										
3-4										
4-5										
5-6										
6-7										
7-8										
8-9										
9-10										
10-11										
11-12										
12-13										
13-14										
14-15										
15-16										
16-17										
17-18										
18-19										
19-20										
20-21										
21-22										
22-23										
23-24										

Figure 8: Sample Sheet for Recording Hourly Averages

3) Using a straight edge, draw a straight line from the adjusted zero at the start of the sampling period to the unadjusted zero at the end of the sampling period as illustrated in Figure 9, page 31. This line represents the zero baseline to be used for the sampling period.

4) Read the zero baseline in percent of chart at the midpoint of each hour interval and record the value on the hourly averages sheet in Figure 8, page 29.

5) Determine the hourly averages by using a transparent object, such as a piece of clear plastic, with a straight edge at least 1 inch long. Place the straight edge parallel to the horizontal chart division lines. For the interval of interest between two vertical hour lines, adjust the straight edge between the lowest and highest points of the trace in that interval, keeping the straight edge parallel to the chart division lines, until the total area above the straight edge bounded by the trace and the hour lines is estimated to equal the total area below the straight edge bounded by the trace and hour lines. See Figure 9 for an illustrated example.

   Read and record on the hourly average sheet the percentage of chart deflection.

   Repeat the above procedure for all the hour intervals for which the analyzer was sampling and which have not been marked invalid. Record all values on the hourly averages sheet in the column headed Reading under "Original."

6) Subtract the zero baseline value (Column 2) from the reading value (Column 1) and record the difference in Column 3.

7) Add the percent zero offset (Column 4) to the difference.

8) Convert percentage chart values to concentration in ppm using the calibration conversion table (in Figure 4) developed from the calibration curve. Record the ppm values in Column 5 on the hourly averages sheet. The "Check" columns will be used in the auditing process and will be discussed in Section 2.2.

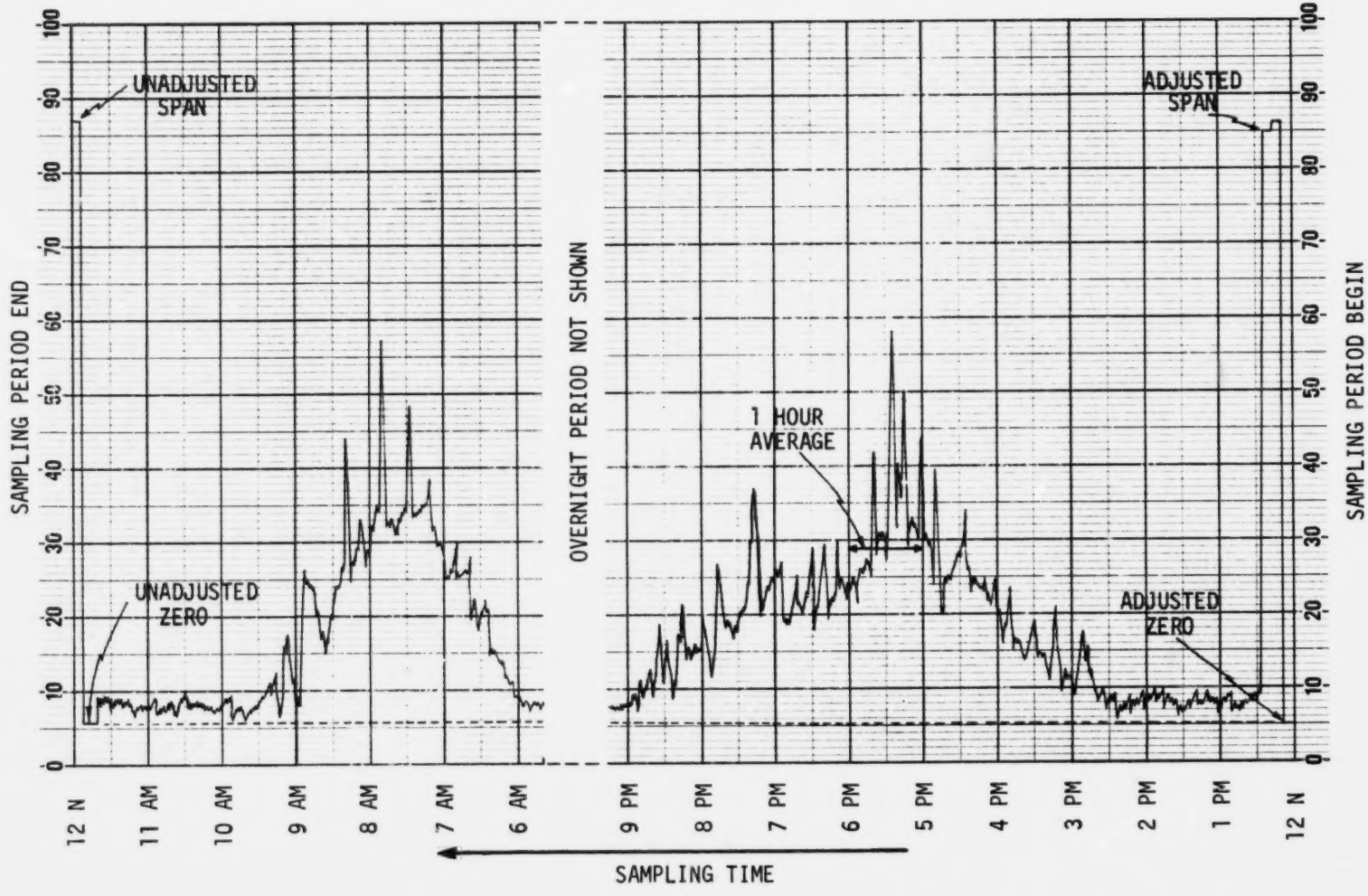

Figure 9: Sample Trace of 24 Hour Sampling Period with Zero and Span Calibrations

Step 19. Data Reporting

Transcribe information and data from the hourly averages sheet to a SAROAD Hourly Data Form (see Figure 10).

Basic instructions for filling out the SAROAD Hourly Data Form are given below. If the data are to be placed in the National Aerometric Data Bank, further instructions can be obtained from the SAROAD Users Manual APTD-0663.

1) The SAROAD Hourly Data Form is an approved form for the recording of data observed on averages at intervals of less than 24 hours. In this case the form is to be used for recording hourly averages of carbon monoxide observations.
2) Entries on the upper left of the form (see sample form, Figure 10) provide indentification (many of these items may already filled in by the time operators receive the cards). These are:
   (1) Agency - group recording the observations.
   (2) City - city in which instrument is operated.
   (3) Site - specific location of the sampler within city.
   (4) Project name, if any.
   (5) Parameter observed - carbon monoxide.
   (6) Time Interval - Hourly.
   (7) Method - Instrumental Nondispersive Infrared.
   (8) Units of Observation - parts-per-million.
3) In the upper right hand corner of the SAROAD Hourly Data Form appears three lines of blocks for coding identifying information. These correspond to the card columns of the numbers beneath each box when punched on an 80-column Hollerith card. EPA will assign codes for the first line of blocks to the reporting agency when Site Identification Forms are initially submitted. They consist of a two-digit code for state (SS), a four-digit code for the area

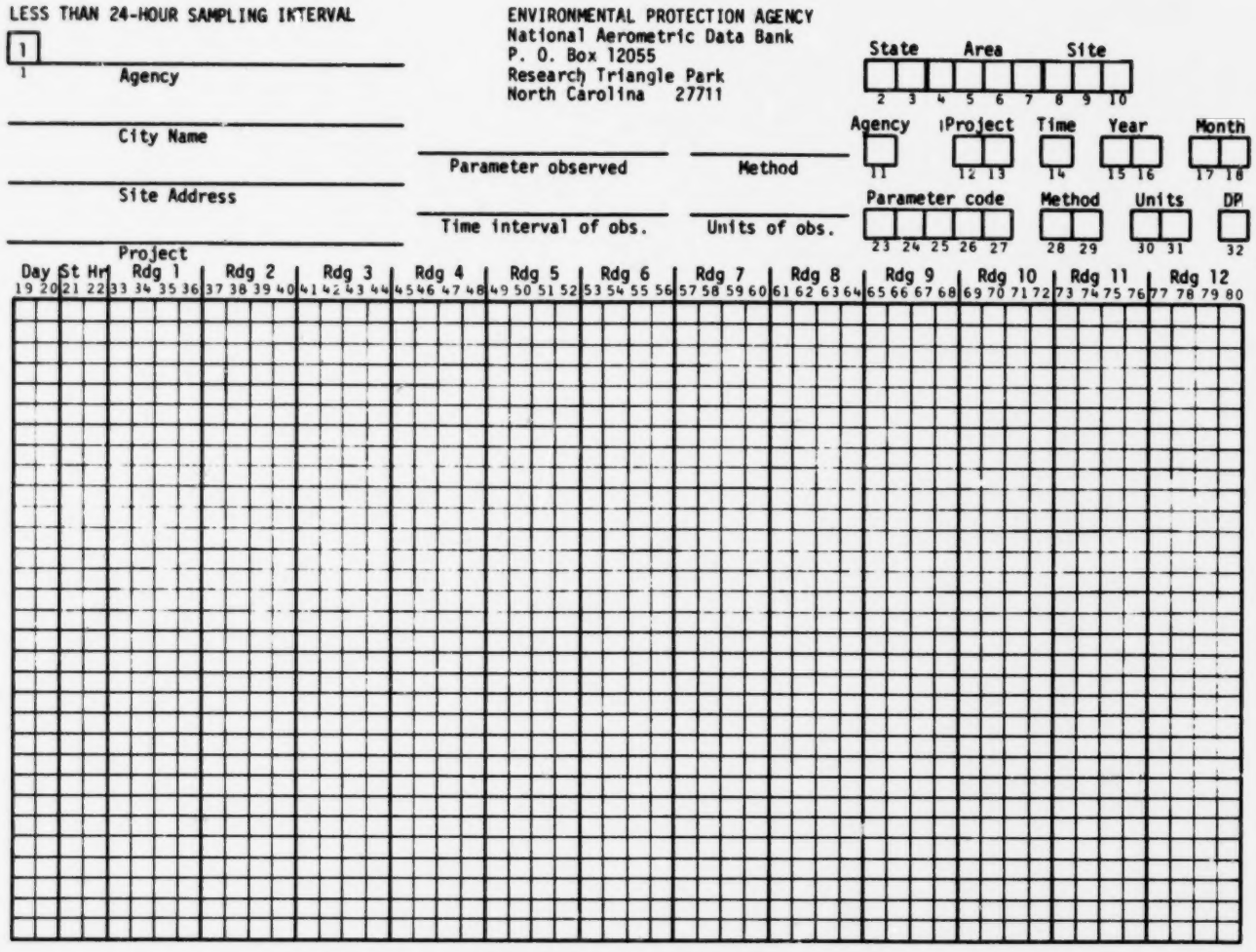

Figure 10: SAROAD Hourly Data Form

of the state in which the sampler is located (CCCC), and a three-digit number specifically identifying the site (XXX). For the remaining two lines of blocks, codes are assigned for each study as follows:

(1) Agency - Agency Code

(2) Project - Project

(3) Time

(4) Year

(5) Month - 01 to 12 for example, as appropriate,

   a. July - 07

   b. August - 08

   c. September - 09

   d. October - 10

   e. November - 11

(6) Parameter Code - 42101

(7) Method - 11

(8) Units - 07

(9) DP - 1 (designates the number of places to the right of the decimal point in the value entries).

4) On the body of the form, the two-block first column, "Day", is the calendar day of the month (e.g., 01, 02). "ST HR" (start hour) calls for either 00 or 12 to denote the starting hour for which data on that line are recorded. Two lines are used for each day's observations. The first line gives "00" (midnight) for "ST HR" and lists the a.m. observations. The next line gives "12" (noon) for "ST HR" and lists p.m. observations.

5) Record the hourly averages in the "Rdg" columns: "Rdg 1" would be for either the 0 to 1 hour reading or the 12 to 13 hour reading; "Rdg 2" would be for either the 1 to 2 hour reading or the 13 to 14 hour reading; etc. In entering the hourly averages, the decimal point is located between the first and second column.

For example:

1.0 ppm would be entered as | | | 1 | 0 |

2.5 ppm would be entered as | | | 2 | 5 | .

Report the results of any special quality control checks performed on special form in Figure 6. Attach the special form for quality control checks to the SAROAD form and give to the supervisor.

File the hourly averages sheet in the data log book.

2.2 Special Checks for Auditing Purposes

In making special checks for auditing purposes, it is important that the check be performed without any special check or adjustment of the system (see section 3.2 for further discussion). Three special checks are required to properly assess data quality. A checking or auditing level of 7 checks out of 100 sampling periods is used here for illustration purposes. The supervisor will specify the auditing level to be used according to monitoring requirements. Each of the three checks is discussed separately.

A. Measuring Control Samples

The operator, when given a control sample (auditing gas) to measure, should proceed as follows:

1) Make no checks or adjustments on the system in preparation of the measurement.

2) Connect the control sample bottle in the system in the same manner that the regular calibration gases are connected (i.e., the control sample should pass through all the analyzer system including the water vapor control unit and the particulate filter).
3) Let the sample gas flow until a stable trace is obtained. Mark the trace with the code number of the control sample and the measured concentration in ppm.
4) Disconnect the control sample gas and connect the regular zero gas to the analyzer.
5) Perform a zero and span calibration as in Step 2B.
6) Remeasure the control sample.
7) Return the control sample bottle and the two (2) measured values, properly identified, to the supervisor. After the supervisor evaluates the results, he may request that the operator perform a multipoint calibration and measure the control sample again.
8) The supervisor fills out and signs the form in Figure 6, page 23.

B. Water Vapor Interference Check

Water vapor checks should be independent and random; that is, a qualified individual other than the regular operator should make the check. Also, the regular operator should not know in advance when the check is to be made. The individual making the check should not adjust, replace, or in any way change the water vapor control unit before performing the check. The exact procedure for performing the check will depend on the type of control being used. Two procedures are given below.

Drying Agent - When a scrubber column filled with a drying agent is used to control water vapor interference, the check can be performed in the following manner.

1) Connect the dry zero gas directly to the analyzer inlet, bypassing the scrubber column. Let the zero gas flow until a stable trace is obtained. Mark the trace as dry zero gas.
2) Remove the segment of line bypassing the drying agent. Place a 50-ml impinger containing 25 ml of distilled water, at room temperature, in the sample line such that the zero gas passes through the impinger, drying agent, and analyzer in that order. CAUTION: With NDIR analyzers having a pressurized cell, this impinger may have to be pressurized. If so, it will have the full cell or pump pressure and will be subject to explosion. Use a pressure vessel of adequate pressure capacity, and avoid the use of glass, if possible.

   Let the gas flow until a stable trace is obtained. Mark the trace as response to saturated zero gas.
3) Determine the difference in the two traces as an equivalent CO concentration in ppm. Always subtract the dry measurement from the saturated measurement. In some cases negative values will result due to normal measurement error. Document the check on the form for reporting quality control checks in Figure 6, page 23, and give to the supervisor for his signature.

Replace or rejuvinate the drying agent if the interference is as large as + 0.5 ppm.

Other Methods - Other methods include refrigeration, refrigeration preceded by humidifier, filter cells, or optical filters. When refrigeration alone is used, the cold trap should be thoroughly drained before the test and the dry zero gas allowed to flow at least 30 minutes before reading. Otherwise, all these methods can be checked in the following manner.

1) Pass zero gas through the system in the same manner as is done in zero and span calibrations. Mark the trace as dry zero gas.
2) Insert a 50-ml impinger filled with 25 ml of distilled water at room temperature into the sample inlet line on the inlet side of the water control unit. CAUTION: With NDIR analyzers having a pressurized cell, this impinger may have to be pressurized. If so, it will have the full cell or pump pressure and will be subject to explosion. Use a pressure vessel of adequate pressure capacity, and avoid the use of glass, if possible.
3) Pass the zero gas through the impinger and system and mark the trace as saturated zero gas.
4) Determine the apparent change in concentration in ppm by subtracting the response to dry gas from the response to saturated gas.
5) Allowable interference levels for different control methods could be specified by the supervisor from method specifications or from the desired accuracy of the reported data.
6) Corrective action should be taken for a measured interference exceeding the allowable level for a particular control unit.

Document the results of the checks on the form in Figure 6, page 23, and forward to the supervisor for his signature.

C. Data Processing Check

In auditing data processing procedures, it is convenient and allows for corrections to be made immediately if checks are made for each sampling period. Hence, rather than check all 24 hourly averages for 7 days out of every 100 days, it is suggested that 2 one-hour averages be checked each

24 hour sampling period. Also, it is suggested that the 2 highest hourly averages or the 2 hours for which the strip chart trace is most dynamic in terms of spikes be selected for checking by scanning the strip chart record. The check must be independent; that is, performed by an individual other than the one who originally reduced the data. The check is made starting with the strip chart record and continuing through the actual transcription of the concentration in ppm on the SAROAD form. This, then, would include reading, calculation, and transcribing or recording errors.

The check is performed in the same manner as the original data were processed as described in Section 2.1, Steps 17 through 19. Values are recorded on the form in Figure 8, page 29, in the "Check" columns. If either one of the two checks differ by as much as $\pm$ 1* ppm from the respective original value, all hourly averages for that sampling period should be checked and corrected. In cases where all hourly averages have been checked, the two original, randomly selected checks should be clearly identified on the hourly averages sheet.

2.3 Special Checks to Detect and/or Identify Trouble

The following checks may be required when: 1) a quality assurance program is first initiated in order to determine the analyzer's performance capabilities and to identify potential problem areas, and 2) at any later time when it becomes increasingly difficult to meet the performance standards of the auditing program to identify and/or evaluate trouble areas. Procedures for performing a zero drift check, flow rate variation sensitivity check, temperature variation sensitivity check, and a voltage variation sensitivity check are discussed individually.

A. Zero Drift Check

If available, set up equipment for monitoring and recording on strip chart the analyzer's power source voltage and the ambient room temperature. If such equipment is not available, use a regular A.C. voltmeter capable of

*For monitoring sites or analyzer configurations where the recorded data do not exhibit frequently occurring sharp spikes, it would be advisable to use a value of $\pm$ 0.5 ppm as the difference above which all hourly averages are rechecked.

measuring between 100 and 130 V.A.C. and connect it across the analyzer power plug. Locate a thermometer or other temperature-indicating device near the analyzer to give a representative reading of the ambient room temperature. Preferably a maximum-minimum thermometer should be used.

1) Connect the zero gas to the analyzer and adjust the trace to 5 percent of chart.
2) Start temperature and voltage recorders or read and record the temperature and voltage each hour for the duration of the test.
3) Let the analyzer operate unadjusted for 24 hours with the zero gas.
4) From the strip chart(s) and recorded data determine the following:
   a) difference between lowest (may be negative) and highest values of the zero trace in ppm as ΔC,
   b) difference between lowest and highest temperatures in °C as ΔT,
   c) difference between lowest and highest line voltages recorded during sampling period in volts as ΔV.
   d) Document the values of ΔC, ΔT and ΔV on the quality control check form in Figure 6, page 23.
5) Compare the fluctuation of the zero trace with the temperature and voltage fluctuations for similarities (i.e., see if the peaks occur at about the same time). If it appears that the zero trace is sensitive to voltage and/or temperature changes, document with a short explanation under data quality statement on the form in Figure 6.

B. Flow Rate Variation Sensitivity Check

1) With the analyzer in normal operating condition, connect a span gas with a concentration corresponding to approximately 80 percent of full scale to the analyzer.
2) Adjust the sample flow and sample cell pressure to the normal operating values and allow time to obtain a stable trace.
3) Mark the trace with flow rate and cell pressure values.
4) Adjust the flow rate to 1/2 of its previous value. Do not readjust the sample cell pressure. Allow time to obtain a stable trace.
5) Mark the trace with flow rate and cell pressure.
6) Adjust the flow rate to 3 times its present setting. Allow time to obtain a stable trace.
7) Mark the trace with flow rate and cell pressure.
8) Record the three flow rate values with corresponding cell pressures and measured concentrations in ppm on the form for quality control checks (Figure 6). Give the form to the supervisor.

C. Temperature Variation Sensitivity Check

From the zero drift check, if $\Delta C \leq 1$ ppm and $\Delta T \geq 6°C$ (11°F), do not perform a temperature sensitivity check. Report temperature sensitivity as $\Delta C/\Delta T$, where ΔC and ΔT are the apparent change in concentration and change in temperature, respectively, as observed from the zero drift check.

If however, the above conditions are not satisfied, perform a temperature sensitivity test as follows:

1) The analyzer is placed in a room where the temperature can be varied by at least $\pm$ 6°C (11°F).
2) Let the analyzer warm up sufficiently to get a stable trace.
3) Set up temperature-measuring device such as a maximum-minimum thermometer near the analyzer.

4) Perform a zero and span calibration at normal room temperature. Reconnect the zero gas to the analyzer.

5) Turn the temperature control down 6°C. Allow time for the room temperature and the analyzer trace to stabilize. Read from the thermometer and record on the strip chart the actual temperature.

6) Turn the temperature control up 12°C from its previous setting (i.e., 6°C above the normal setting). Allow time for room temperature and analyzer to stabilize. Record actual temperature on the strip chart.

7) Calculate

$$\frac{\Delta C}{\Delta T} = \frac{C_{T_1} - C_{T_2}}{T_1 - T_2}$$

where

C_{T_1} = concentration measured at T_1,

C_{T_2} = concentration measured at T_2,

T_1 = highest temperature (centigrade),

T_2 = lowest temperature (centigrade),

and

$\frac{\Delta C}{\Delta T}$ = apparent change in concentration per °C change in temperature.

Document the test on the form for reporting quality control checks in Figure 6, page 23.

D. Voltage Variation Sensitivity Test

From the zero drift check, if $\Delta C \leq 1$ ppm and $\Delta V \geq 10$ volts, do not perform a voltage variation sensitivity check. Report voltage sensitivity as $\Delta C/\Delta T$, where ΔC and ΔV are the actual values observed from the zero drift check.

If however, results from the zero drift check do not fall in the above category, perform a voltage variation sensitivity test as follows:

1) Plug the analyzer into a variac capable of adjusting the power line voltage by $\pm$ 15 volts from the normal line voltage and plug the variac into the regular electrical outlet.
2) Connect a voltmeter across the variac output leads.
3) Perform a regular zero and span calibration with the variac adjusted so that the voltmeter reads 115 volts.
4) With the span gas still connected, adjust the variac until the voltmeter reads 105 volts. Allow the analyzer to stabilize. Identify that portion of the strip chart trace as being at 105 volts.
5) Adjust the variac until the voltmeter reads 125 volts. Allow the analyzer to stabilize and properly identify the trace.
6) Read the trace deflection at 105 and 125 volts and convert to concentration in ppm.
7) Calculate the change in concentration per unit change in voltage.

$$\frac{\Delta C}{\Delta V} = \frac{C_{125} - C_{105}}{20}$$

where

C_{125} = the measured concentration at 125 volts,

C_{105} = the measured concentration at 105 volts,

and

$\frac{\Delta C}{\Delta V}$ = the change in concentration per unit change in voltage.

Results from the flow rate, temperature, and voltage sensitivity checks and estimates (could be actual measurements, if available) of the maximum expected variation of each of the parameters under normal operational

conditions are recorded in Table 1. The maximum expected error for each parameter is computed as illustrated in Table 1. Assumed values of expected variation are given for ambient room temperature as $\pm$ 4.5°C from a set value and for voltage as $\pm$ 12 volts from a normal 115 volt source. Variation in flow rate will depend on the analyzer. A maximum expected variation in Q can be determined by taking the 3σ value of flow rate changes from 20 to 30 sampling periods. A fourth important parameter is water vapor interference. There are only two values for water vapor interference as tested herein. They are dry and saturated (see Section 2.2, B for this check); therefore, the value, $\frac{\Delta C}{\Delta W}$, represents the maximum interference that is expected to occur and may not be representative of error in the measured data in areas characterized by low relative humidities. Table 1 should be completed for each analyzer and made a part of the operational data log book.

Table 1: Analyzer Evaluation Data

Variable	Measure of Sensitivity	Maximum Expected Variation	Maximum Expected Error
Flow Rate	$\frac{\Delta C}{\Delta Q}$ =	ΔQ =	$\frac{\Delta C}{\Delta Q} \times \Delta Q$ =
Temperature	$\frac{\Delta C}{\Delta T}$ =	ΔT = 9°C	$\frac{\Delta C}{\Delta T} \times \Delta T$ =
Voltage	$\frac{\Delta C}{\Delta V}$ =	ΔV = 24 V	$\frac{\Delta C}{\Delta V} \times \Delta V$ =
Water Vapor			$\frac{\Delta C}{\Delta W}$ =

2.4 Calibration of Sample Flow and Sample Cell Pressure Indicators

A. Flow Rate Calibration

Rotameters usually require cleaning every six months to a year. It is suggested that they be calibrated after having been cleaned or at any sign of erratic behavior. Calibration can be accomplished using a wet test meter as a secondary standard or a rotameter which has been recently calibrated against a secondary standard.

The easiest method is to use a calibrated rotameter as follows:

1) Place the calibrated rotameter in series with the rotameter to be calibrated and adjust the flow rate as read on the calibrated rotameter to 80 percent of full scale.
2) Adjust, if necessary, the test rotameter until it reads the same as the calibrated rotameter and lock the adjustment screw or knob.
3) Work down scale stopping at 65, 50, 35, 20 and 5 percent of full scale. Record corresponding readings from both rotameters on a rotameter calibration sheet.
4) Using the calibration curve for the calibrated rotameter, construct a calibration curve of rotameter reading versus flow rate for the test rotameter.

B. Sample Cell Pressure Gauge Calibration

It is suggested that initially the sample cell pressure gauge be calibrated at 6-month intervals or at any sign of erratic behavior of the gauge, such as a change larger than $\pm$ 6.9 $\times$ 10^3 Nm^{-2} (1 psi) in the sample cell pressure during a sampling period in which the sample flow rate did not change by more than $\pm$ .014 m^3/hr (0.5 ft^3/hr). If after two 6-month calibrations the gauge shows no sign of change (i.e., reads within $\pm$ 6.9 $\times$ 10^3 Nm^{-2} (1 psi) of the calculated pressure), go to once a year calibrations. Repeat the process making the period shorter or larger according to the magnitude of change of the gauge until an optimum calibration interval is realized.

One means of performing the calibration is using a bottle of zero gas, the gauge to be calibrated, and a mercury manometer in a set-up as shown in Figure 11. With this set-up the gauge can be calibrated from atmospheric pressure up to 2.07×10^5 Nm^{-2} (30 psi), usually 100 percent of its range, in the following manner:

1) Open cylinder pressure valve.
2) Adjust secondary pressure regulator until the secondary pressure gauge reads 1.38×10^5 Nm^{-2} (20 psi).
3) Open the manometer valve slowly and let manometer stabilize.
4) Open gauge valve slowly, let test gauge stabilize.
5) Read the difference in the mercury columns (h) in centimeters.
6) Determine ambient atmospheric pressure (P_r) from a calibrated wall barometer, or other suitable barometer, in Newtons per square meter (Nm^{-2}).
7) Compute the pressure at the test gauge (P_m) in Nm^{-2} by

$$P_m(Nm^{-2}) = 7.5 \times 10^{-4} \times h(\text{cm Hg}) + P_r(Nm^{-2})$$

$$(P_m(\text{psi}) = 5.17 \times h(\text{cm Hg}) + P_r(\text{psi})) .$$

8) Record the computed value of P_m and the actual reading of the test gauge.
9) Repeat Procedures 2 through 8 with the secondary pressure gauge reading 1.72×10^5 Nm^{-2} (25 psi) and then 2.07×10^5 Nm^{-2} (30 psi).
10) Construct a calibration curve of gauge reading versus computed pressure for the gauge.

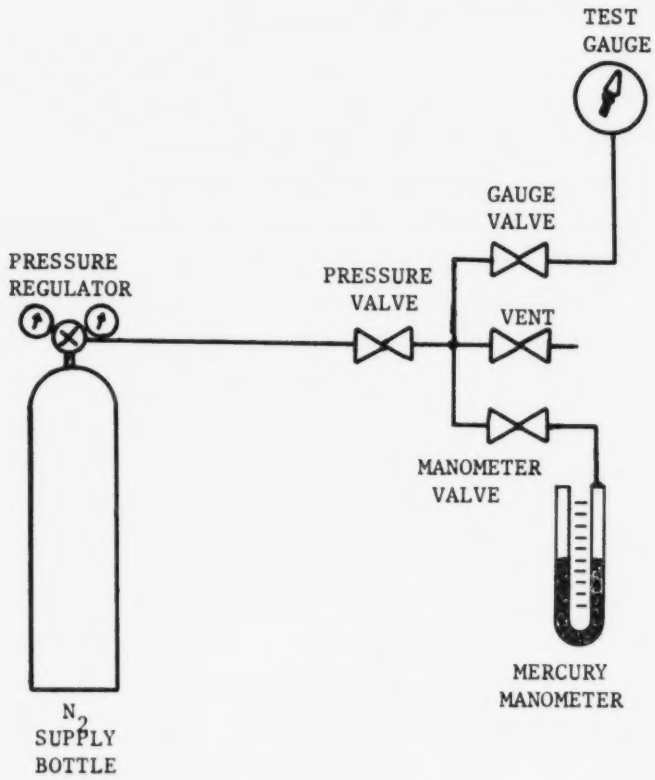

Figure 11. Calibration Set-up for Pressure Gauges

2.5 Facility and Apparatus Requirements

A. Facility

A weatherproof shelter or room is required for housing the NDIR analyzer. Ideally the shelter or room would be equipped with an automatic all seasons air conditioning unit capable of maintaining a pre-set temperature within ± 3°C (5°F). It is desirable that the heating/cooling be done electrically to guard against the station's emitting pollutants and altering the ambient air quality. A heat pump or a cooling unit with electric resistance heaters would be suitable.

The shelter must be large enough to house the analyzer, any data acquisition equipment, and storage space for the calibration gases. It should also have adequate working space for the inspection, calibration, and maintenance of the system.

B. Apparatus

Items of equipment with approximate costs are listed in Table 2. Costs associated with the analyzer, sample introduction system, and water vapor control unit vary according to the analyzer model and make, size of the sampling station, and type of water vapor control unit used; hence, only approximate ranges of cost are given for these items.

The calibration gases are for size 1A cylinders, certified to an accuracy of ± 2% of the stated CO concentration as determined by analysis.

Audit gases used as control samples are certified to an accuracy of ± 1% of the stated CO concentration and for mobility can be obtained in size 3 cylinders.

Each item is checked according to whether it is 1) required in the reference method, 2) used to control a variable or parameter, 3) required for auditing purposes, or 4) used to monitor a variable.

Table 2: Apparatus Used in the NDIR Method

Item of Equipment	Approx Cost 1972	Associated Error	Reference Method	Variable Control	Auditing Equipment	Variable Monitoring
Apparatus						
1. Carbon Monoxide Analyzer	2 to 4,000		✓			
2. Sample Introduction System			✓			
3. Water Vapor Control Unit			✓			
4. Strip Chart Recorder	1,000					
Reagents						
5. Zero Gas (1 bottle)	13	Calibration	✓			
6. Calibration gases (4 bottles)	204	Calibration	✓			
Optional Equipment						
7. 3 Primary Standards (Spiked Samples)	393	Total Measurement Error			✓	
8. 2-Stage Pressure Regulator	96				✓	
9. Midget Impinger	35	Water Vapor Interference			✓	
10. Temperature Control (Heating/ Cooling System)	1,000	Zero Drift		✓		
11. Diffusion Chamber	10	Data Reduction		✓		
12. Constant Voltage Regulator	270	Zero Drift		✓		
13. A.C. Voltmeter	50	Zero Drift				✓
14. Maximum Minimum Thermometer	35	Zero Drift				✓

PART II. SUPERVISION MANUAL

3.0 GENERAL

Consistent with the realization of the objectives of a quality assurance program as given in Section 1.0, this manual provides the supervisor with brief guidelines and directions for:

1) the collection and analysis of information necessary for the assessment of NDIR data quality,
2) isolating, evaluating, and monitoring major components of system error,
3) changing the physical system to achieve a desired level of data quality,
4) varying the auditing or checking level to achieve a desired level of confidence in the validity of the outgoing data, and
5) selecting monitoring strategies in terms of data quality and cost for specific monitoring requirements.

This manual provides brief directions that cannot cover all situations. For somewhat more background information on quality assurance see the Management Manual of this document. Additional information pertaining to the NDIR method can be obtained from the final report for this contract and/or from the literature referenced at the end of the Management Manual.

Directions are written in terms of a 24-hour sampling period and an auditing level of n=7 checks out of a lot size of N=100 for illustration purposes. Information on different auditing levels is given in the Management Manual.

Specific actions and operations required of the supervisor in implementing and maintaining a quality assurance program as discussed in this Manual are summarized in the following listing.

1) Data Assessment
   a) Set up and maintain an auditing schedule.
   b) Qualify audit results (i.e., insure that checks are independent and valid).
   c) Perform necessary calculations and compare to suggested performance standards.
   d) Make corrections or alter operations when standards are exceeded.
   e) Forward acceptable qualified data, with audit results attached, for additional internal review or to user.

2) Routine Operation
   a) Obtain from the operator immediate reports of suspicious data or malfunctions. Initiate corrective action or, if necessary, specify special checks to determine the trouble; then take corrective action.
   b) On a daily basis, evaluate and dispose of (i.e., accept or reject) data that have been identified as questionable by the operator.
   c) Examine operator's log books periodically for completeness and adherence to operating procedures.
   d) Approve data sheets, calibration data, etc., for filing by operator.
   e) File auditing results.

3) Evaluation of Operations
   a) Evaluate available alternative monitoring strategies in light of your experience and needs.
   b) Evaluate operator training/instructional needs for your specific operation.

3.1 Assessment of NDIR Data

A. Required Information

A valid assessment of a batch or lot of NDIR data can be made at a given level of confidence with information derived from three special checks. The three checks are:

1) measurement of control samples,
2) water vapor interference check, and
3) data processing check.

Directions for performing the checks are given in the Operations Manual, Section 2.2. Directions for insuring independence and proper randomization in the auditing process and for the analysis of the results are presented in this section.

B. Collection of Required Information

1) Measurement of Control Samples

Acquisition of Control Samples - obtain at least three audit gases, for use as control samples, that have been assayed and certified to be within ± 1 percent of the stated level of CO. The three levels should be selected to span the range from about 5 to 40 ppm. The specific values should be varied as new control samples are purchased. Code each control sample and record the code and certified concentration value in a log book which is not accessible to the operator(s). Use these coded audit gases as control samples.

Procedure for Performing Check - From the next 100 sampling periods* randomly select 7 periods** (e.g., one period selected randomly from seven intervals of fourteen sampling periods each would be satisfactory). Then randomly select an hour for each of the 7 periods (it is felt that one hour randomly selected from the 8-hour working day will adequately satisfy the requirements).

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*One sampling period is defined as one 24-hour day.

**The extent of auditing, i.e., the number of checks, will be discussed in the Management Manual.

At the selected hour within the appropriate sampling period, have the operator measure one of the control samples (i.e., one of the three audit gases). Instruct the operator to make no checks or adjustments on the system before making the measurement. A control sample can be reused several times as long as the operator does not know the true concentration. The operator performs the measurement according to the procedures given in the Operations Manual, Section 2.2.A.

Treatment of Data - Two values are reported from each check. One value represents the measured value of the control sample with no adjustments made to the system prior to measurement. The second reported value is the measure of the control sample obtained after a zero and span calibration has been performed. Results of the second measurement (i.e., the measurement made after a zero and span calibration has been performed) are used to detect and identify trouble and are discussed in Section 2.4. Results of the first measurement are used in assessing data quality and are treated below.

For each measurement or check, compute the difference in the true or certified concentration, C_o, and the measured concentration, C_a, in ppm as

$$d_{li} = C_{ai} - C_{oi}$$

where

i is the i^{th} time that the check has been made during a given auditing period.

2) Water Vapor Interference Check

Procedure for Performing Check - Using the same seven sampling periods as were randomly selected in 1 above, conduct an independent (i.e., done by someone other than the regular operator) water vapor interference check without forewarning of the operator. Perform the check according to instructions given in the Operations Manual, Section 2.2.B. To insure

unbiased checks, it is recommended that the individual performing the checks be changed periodically and that the results from successive checks be evaluated by the supervisor for reasonableness in terms of individual magnitudes and variations in magnitude between checks.

Treatment of Data - For each measurement or check, compute the difference in instrument response to dry zero gas, C_d, and saturated zero gas, C_s, in ppm as

$$d_{2i} = C_{si} - C_{di}$$

where

i is the i^{th} time that the check has been made during a given auditing period.

3) Data Processing Check

Procedure for Performing Check - Independent checks on data processing errors are made as directed in the Operations Manual, Section 2.2.C. Data processing checks are made each sampling period (24 hours). To insure continuous unbiased checks, it is recommended that the individual performing the checks be changed periodically.

Treatment of Data - Two checks are made each sampling period. For each check determine the difference between the check value and the original value. If either check differs by as much as $\pm$ 1 ppm from the original value, all hourly averages for that period are checked and corrected. For reporting data quality, the value used for correcting all hour averages (e.g., $\pm$ 1 ppm) is reported. In situations where the procedure in Section 4.1 of the Management Manual is to be followed for data quality assessment, compute a value for reporting on the form in Figure 12 by

a) subtracting the check value in ppm from the original value in ppm for each of the two hourly averages that were originally selected for checking.

b) adding the two values computed in a) above algebraically (i.e., keep track of the signs) and dividing by 2, and

c) reporting the result as

$$d_{3i}$$

where

i is the i^{th} audit performed during the auditing period.

C. Treatment of Collected Information

1) Identification of Defects

One procedure for identifying defects is to evaluate auditing checks in pairs, i.e., $d_{11}d_{21}$, $d_{12}d_{22}$, $d_{13}d_{23}$ ---, $d_{17}d_{27}$. If one or both members of the pair are defective, it counts as one defect. No more than one defect can be declared per set. Data processing errors should be corrected when found, and are not, therefore, discussed here.

Any set of auditing checks in which the value of d_{1i} or d_{2i} is greater than $\pm$ 2.2 ppm or + 1.7 ppm, respectively, will be considered a defect. These values are assumed to be the 3σ values and are discussed in Section 3.2. As data become available, these limits should be reevaluated and adjusted, if necessary. Small (e.g., less than 0.4 ppm) negative values of d_{2i} may occur as a result of measurement error.

2) Reporting Data Quality

Each lot of data submitted with SAROAD forms or tapes should be accompanied by the minimum data qualifying information as shown in Figure 12. The individual responsible for the quality assurance program should sign and date the form. As an illustration, values from Section 3.2, Suggested Standards for Judging Performance, are used to fill in the blanks in Figure 12. The reported auditing rate is the rate in effect at

Supervisor's Signature _____ Reporting Date _____

Auditing Rate for Data Errors: n = 7 , N = 100

Definition of Defect: $|d_{1i}| \geq 2.2$ ppm, $d_{2i} \geq 1.7$ ppm

Auditing Rate for Data Processing Errors: n = 2 , N = 24

Definition of Defect*: $|d_{3i}| \geq 1$** ppm

Number of Defects Reported _____ (should be circled in the table below)

Audit	Check Values (ppm)						
1. Measurement of Control Samples (d_{1i})	d_{11}	d_{12}	d_{13}	- - - - - -	d_{1i}	---	d_{1n}
2. Water Vapor Interference Check (d_{2i})	d_{21}	d_{22}	d_{23}	- - - - - -	d_{2i}	---	d_{2n}
3. Data Processing Check (d_{3i})	d_{31}	d_{32}	d_{33}	- - - - - -	d_{3i}	---	d_{3n}

*Data processing errors are corrected when found and are, therefore, not reported as defects.

**This is actually the value of one check while d_{3i} is the average of two checks.

Figure 12: Data Qualification Form

the beginning of the auditing period. An increase or decrease in auditing rate during the auditing period will be reflected by the total number of checks reported. The reason for change should be noted on the form.

Check values (i.e., d_{1i}'s, d_{2i}'s and d_{3i}'s) are calculated as directed in Section 3.1.B and reported in ppm. Values of d_{3i} need be reported only if requested by the Manager. All reported check values exceeding the definition of a defect should be marked for easy recognition by circling on the form.

Attach the data qualification form to the SAROAD form and forward for additional internal review or to the user.

3.2 Suggested Standards for Judging Performance

Results from a collaborative test of the NDIR method (Ref. 1) show that system precision is a function of the CO concentration. The performance standard given below in Table 3 for measurement of control samples was taken from the point of maximum system precision which occurred at a concentration of about 17 ppm. The value of $\pm$ 2.2 ppm represents the 3σ limit. This standard should be reevaluated and adjusted for different concentration levels when data collected from the measurement of control samples, as directed in Section 2.2 of the Operations Manual, become available.

The suggested standards given for water vapor interference and data processing errors are no more than rough estimates. Reasonable performance standards can be determined as data become available from the auditing program.

3.3 Collection of Information to Detect and/or Identify Trouble

In a quality assurance program one of the most effective means of preventing trouble is to respond immediately to reports from the operator of suspicious data or equipment malfunctions. Application of proper corrective actions at this point can reduce or prevent the collection of poor quality data. Important error sources, methods for monitoring applicable variables, and suggested control limits for each source are discussed in this section.

Table 3: Suggested Performance Standards

Standards for Defining Defects

1. Measurement of Control Samples; $d_{1i} \geq \pm 2.2$ ppm
2. Water Vapor Interference Check; $d_{2i} \geq 1.7$ ppm

Standard for Correcting Data Processing Errors

3. Data Processing Check; $|d_{3i}| \geq 1$ ppm

Standards for Audit Rates

4. Suggested minimum auditing rates for data error; number of audits, n = 7; Lot size, N = 100; allowable number of defects per lot, d = 0.
5. Suggested minimum auditing rates for data processing error; number of audits, n = 2; lot size, N = 24; allowable number of defects (i.e., $|d_{3i}| \geq 1$ ppm) per lot, d = 0.

Standards for Operation

6. If at any time d = 1 is observed (i.e., a defect is observed) for either d_{1i} or d_{2i}, increase the audit rate to n = 20, N = 100 until the cause has been determined and corrected.
7. If at any time d = 2 is observed (i.e., two defects are observed in the same auditing period), stop collecting data until the cause has been determined and corrected. When data collection resumes, use an auditing level of n = 20, N = 100 until no defects are observed in three successive audits.
8. If at any time either one of the two conditions listed below is observed, 1) increase the audit rate to n = 20, N = 100 for the remainder of the auditing period, 2) perform special checks to identify the trouble area, and 3) take necessary corrective action to reduce error levels. The two conditions are:
   a) two (2) d_{1i} values exceeding $\pm$ 1.4 ppm, or
      three (3) d_{1i} values exceeding $\pm$ 0.7 ppm
   b) two (2) d_{2i} values exceeding $\pm$ 1.0 ppm, or
      three (3) d_{2i} values exceeding $\pm$ 0.5 ppm.

A. Identification of Important Variables

A great many variables can affect the expected precision and accuracy of measurements made by the NDIR method. Certain of these are related to analysis uncertainties and others to instrument characteristics. Major sources of error are discussed below.

Inaccuracy and Imprecision in the Stated CO Concentration of Calibration Gases (Ref. 1) - There are two components of error involved; one is the error in the original assay, and the second is due to the deterioration of CO with time.

Large errors in the original assay should be detected when the gas is first purchased by measuring with a properly calibrated and functioning analyzer. Changes in concentration occurring as a function of time will be detected at a given level when spiked samples can no longer be measured within given limits with a properly calibrated and functioning analyzer.

Water Vapor Interference - Water vapor is a positive interference for all NDIR analyzers (Refs. 1-5). The magnitude of the interference is a function of the type of control equipment being used and the operational state of the equipment.

Refrigeration and drying agents have proved to be effective in controlling water vapor interference (Ref. 1). Refrigeration units should be preceded by a humidifier when used in locations where the dewpoint of the ambient air is frequently below the dewpoint in the refrigeration unit. Drying agents have to be checked and replaced frequently when used in areas characterized by high relative humidities (Ref. 4).

Error due to water vapor interference is not compensated for or corrected by the zero and span calibrations. Its magnitude is monitored as part of the auditing program by performing periodic water vapor interference checks.

Data Processing Errors - Data processing, starting with reducing the data from a strip chart record through the act of recording the measured concentration on the SAROAD form, is subject to many types of errors. Perhaps the major source of error is in reading hourly averages from the strip chart record. This is a subjective process and even the act of checking a given hourly average does not insure its absolute correctness. The approach used in Section 2.2.C of the Operations Manual means that one can be about 55% confident that no more than 10% of the reported hourly averages are in error by more than $\pm$ 1 ppm.

The magnitude of data processing errors can be estimated from, and controlled by, the auditing program through the performance of periodic checks and making corrections when large errors are detected. A procedure for estimating the bias and standard deviation of processing errors is given in Section 4.1 of the Management Manual.

Zero Drift - Zero drift is defined as the change in instrument output over a stated period of time, usually 24 hours, of unadjusted, continuous operation when the input concentration is zero.

Several variables contribute to zero drift. Some variables such as variations in ambient room temperature, source voltage, and sample cell pressure result in a zero drift that is not linear with time. Therefore, performing a zero and span calibration does not correct for the component of drift throughout the sampling period but rather just at the time the calibration is performed.

Degradation of electronic components and increased accumulation of dirt in the sample cell may result in a zero drift that is linear with time. Periodic zero and span calibrations allow for correction of this component of zero drift for the entire sampling period.

The importance of zero drift to data quality can be determined from the results obtained from measuring control samples. If a zero and span calibration is nearly always required in order

to measure a control sample within desired limits (see Section 2.1), a zero drift check as described in section 2.2 should be performed to determine the characteristics and major causes of the drift. For a drift that is generally linear with time, it is valid to perform a zero and span before measuring control samples as part of the auditing process. However, if the drift is a function of variations in temperature, voltage, or pressure, as can be determined by the special checks in section 2.2, zero and span calibrations should not be performed before measuring control samples for auditing purposes. In this case meeting desired performance standards may require more frequent zero and span calibrations or more rigid control of temperature, voltage, and pressure, as appropriate.

Span Drift - Span drift is defined as the change in instrument output over a stated time period of unadjusted, continuous operation when the input concentration is a stated upscale value. For most NDIR analyzers the major component of span drift is zero drift and is corrected or controlled as discussed above. The component of span drift other than zero drift can be caused by either optical or electronic defects. If this component of span drift is large or shows a continuous increase with time, the manufacturer's manual should be followed for troubleshooting and correction of the defect. The importance or magnitude of span drift can be determined from the zero and span calibrations after each sampling period.

Excessive Noise - Noise is defined as spontaneous deviations from a mean output not caused by input concentration changes. Excessive noise may result when an analyzer is exposed to mechanical vibrations. Other sources of noise include a high gain setting on the recorder, accumulation of dirt on sample cell walls and windows, or loose dirt in the sample cell (Ref. 6).

Excessive noise is evidenced by either an extra broad strip chart trace or a narrow but erratic trace. The manufacturer's manual should be followed for troubleshooting and correcting the cause.

B. How to Monitor Important Variables

System noise, zero drift, span drift, and sample cell pressure are monitored as part of the routine operating procedures. Implementing an auditing program effectively monitors calibration gas concentration, water vapor interference, and data processing errors. Variations in ambient room temperature and/or source voltage can be monitored with a minimum-maximum thermometer and an a.c. voltmeter, respectively. Table 4 summarizes the variables and how they can be monitored.

Table 4: Methods of Monitoring Variables

Variable	Method of Monitoring
1. Calibration Gas Concentration	Measurement of control samples as part of the auditing program.
2. Water Vapor Interference	Water vapor interference checks performed as a part of the auditing program.
3. Data Processing Errors	Data processing checks performed as a part of the auditing program.
4. Zero Drift	Zero check and adjustment before each sampling period as part of routine operating procedure.
5. Span Drift	Span check and adjustment before each sampling period as part of routine operating procedure.
6. System Noise	Check of strip chart record trace for signs of noise after each sampling period as part of routine operating procedure.
7. Sample Cell Pressure Variation	Reading and recording sample cell pressure at the beginning and end of a sampling period as part of routine operating procedure.
8. Temperature Variation	Minimum maximum thermometer placed near the anlayzer, or any other temperature-indicating device, read periodically throughout the sampling period. This would usually be done as a special check.
9. Voltage Variation	A.C. voltmeter measuring the voltage to the analyzer and read periodically throughout the sampling period. This would usually be done as a special check.

C. Suggested Control Limits

Appropriate control limits for individual variables will depend on the level of performance needed. Table 5 gives suggested performance standards for measuring control samples and water vapor interference. The standards are given in terms of a mean (bias) and standard deviation.

Standards given for the measurement of control samples were taken from the results of a collaborative test (Ref. 1). The standard deviation, σ_1, is actually a function of the CO concentration and should be evaluated for different levels as the necessary data become available. The value used here is probably adequate for concentration values between 8 and 30 ppm.

In the table, error in measuring control samples has been divided into four components. They are: 1) error in calibration gas concentration, 2) zero drift, 3) span drift, and 4) noise. The values given for the various error components were arrived at in the following way. Verification of calibration gas concentrations can be made, at the 3σ level, within $\pm$ (1.0 + 0.02 C_c)ppm by measuring on a properly calibrated and functioning analyzer. This would result in an upper limit of $\pm$ 1.2 ppm for a calibration gas with a true concentration of 10 ppm. Any deviation larger than $\pm$ 1.2 ppm indicates that the CO concentration value has actually changed with time from the certified value and the gas should be reassayed.

The nonlinear component of zero drift which can result from variations in temperature, pressure, or voltage is not totally corrected for by zero and span calibrations. If the zero drift is randomly positive and negative from sampling period to sampling period, the drift probably has a large nonlinear component. From previous experience with NDIR analyzers, a $\pm$ 1.2 ppm nonlinear zero drift over a 24-hour sampling period is believed to be a reasonable upper limit.

The effect of span drift, that component other than zero drift, is a function of the CO concentration level being measured. This component of drift is normally small and is usually measured at about 80 percent of full scale. The effect, then, in this case would be the ratio of the CO concentration being measured and 40 ppm (80 percent of scale) times the drift in ppm.

Table 5: Suggested Control Limits for Parameters and/or Variables

Parameter/Variable	Suggested Performance Standard		
	Mean	Standard Deviation (ppm)	Upper Limit (3σ)
1. Measurement of Control Samples	$\bar{d}_1 = .025C_a$*	$\sigma_1 = 0.72$	$\pm$ 2.16
Calibration Gas Concentration Error	$\bar{d}_a = .025C_c$**	$\sigma_a = 0.4$	$\pm$ 1.2
Zero Drift (Non-Linear Component)	$\bar{d}_b = 0$	$\sigma_b = 0.4$	$\pm$ 1.2
Temperature Variations Voltage Variations Cell Pressure Variations			
Span Drift (other than zero drift)	$\bar{d}_c = 0$	$\sigma_c = 0.2$	$\pm$ 0.6
Noise	$\bar{d}_d = 0$	$\sigma_d = 0.2$	$\pm$ 0.6
Total: $\sigma_1' = \sqrt{\sigma_a^2 + \sigma_b^2 + \sigma_c^2 + \sigma_d^2}$	$\bar{d}_1' = .025C_a$	$\sigma_1' = 0.67$	$\pm$ 2.01
2. Water Vapor Interference	$\bar{d}_2 = 0.3$	$\sigma_2 = 0.3$	+ 1.74

*C_a = concentration of control sample

**C_c = concentration of calibration gas

It is estimated that this component of drift very seldom introduces an error as large as $\pm$ 0.6 ppm and on the average accounts for less than $\pm$ 0.2 ppm error in the measured value.

System noise can originate in the analyzer or recorder. Specifications on most analyzers quote a maximum noise level of $\pm$ 1 percent of full scale or $\pm$ 0.5 ppm for a 0 to 50 ppm scale. With proper maintenance the combined noise levels of analyzer and recorder should seldom exceed an equivalent concentration of $\pm$ 0.6 ppm.

Combining the means and standard deviations of component errors as

$$\bar{d}_1' = \bar{d}_a + \bar{d}_b + \bar{d}_c + \bar{d}_d ,$$

and

$$\sigma_1' = \sqrt{\sigma_a^2 + \sigma_b^2 + \sigma_c^2 + \sigma_d^2}$$

shows that at this level of control the suggested performance standard for measuring control samples is satisfied as is evidenced by

$$\bar{d}_1' = \bar{d}_1 = 0.025\ C_t$$

and

$$\sigma_1' \simeq \sigma_1 .$$

Water vapor is a positive interference for NDIR CO monitors. Standards given here are strictly estimates and should be reevaluated and adjusted for different types of control units as data become available. Here it is assumed that interference errors have a negative exponential distribution whose mean, $\bar{d}_2$, and standard deviation, σ_2, are equal to 0.3 ppm. The 3σ and 2σ limits for such a distribution are 1.74 ppm and 0.9 ppm, respectively. The values given for $\bar{d}_2$ and σ_2, then, would indicate that on the average 99.7 percent of the time the interference would be between 0 and 1.74 ppm, 95 percent would be between 0 and 0.9 ppm, and 74 percent between 0 and 0.3 ppm to satisfy the suggested standard. These values are, of course, for controlled conditions. If the water vapor control unit is not properly maintained, much larger errors could result. Negative values for water vapor interference may be observed due to measurement error.

3.4 Procedures for Improving Data Quality

Quality control procedures designed to control or adjust data quality may involve a change in equipment or in operating procedures. Table 6 lists some possible procedures for improving data quality. The applicability or necessity of a procedure for a given monitoring situation will have to be determined from results of the auditing process or special checks as performed to identify the important variables. The expected results are given for each procedure in qualitative terms. If quantitative data are available or reasonably good estimates can be made of the expected change in data quality resulting from implementation of each procedure, a graph similar to that in Figure 18, Section 4.3 of the Management Manual can be constructed. The values used in Table 13 and Figure 18 are assumed and were not derived from actual data.

Equipment and personnel costs are estimated for each procedure. Personnel costs were taken as 5 dollars per hour for operator time and 10 dollars per hour for supervisor time. Equipment costs were prorated over 5 years for continuous monitoring, i.e., sampling 365 days a year. All costs are for a lot size of 100, that is, 100 days of sampling.

A procedure for selecting the appropriate quality control procedure to insure a desired level of data quality is given below:

1) Specify the desired performance standard, that is, specify the limits within which you want the deviation between the measured and the true concentration to fall a desired percentage of the time. For example, to measure within $\pm$ 3 ppm 95 percent of the time, the following performance standards must be satisfied:

$$\left|\hat{\tau} \pm 2\hat{\sigma}_T\right| \leq 3 \text{ ppm.}$$

2) Determine the system's present performance level from the auditing process, as described in Section 4.1

Table 6: Quality Control Procedures or Actions

Procedure	Description of Action	Expected Results	Costs		
			Equip	Personnel	Total
A1. Verify concentration of calibration gas	a) Verify concentration of new calibration gas as described in Section 2.1 of the Operations Manual. If certified and measured values differ by more than $\pm(1.0 + 0.02\ C_c^*)$ppm, reject the gas.	Reduces likelihood of calibration gas errors exceeding $\pm(1.0 + 0.02\ C_c)$ppm.	$70	$20	$90
	b) Verify concentration of calibration gas anytime a control sample cannot be measured within $\pm(1.0 + 0.01\ C_a^{**})$ppm after the analyzer has been calibrated and is in proper working order.				
A2. Replicate calibration curve	Repeat the calibration process after one day and use the average of each pair (other than 0 and span) to construct a calibration curve.	Reduces random error calibration points (other than 0 and span) by $\frac{1}{\sqrt{2}}$ and detects large errors made in original replicate.		40	40

*C_c = certified concentration of calibration gas

**C_a = certified concentration of control sample

Table 6: Quality Control Procedures or Actions (Cont'd)

Procedure	Description of Action	Expected Results	Costs		
			Equip	Personnel	Total
A3. Perform multipoint calibrations	Perform multipoint calibration when deviation between measured and stated value of control sample differs by more than $\pm(1.0 + 0.01\ C_a)$ when measured immediately after a zero and span calibration.	Reduces errors due to a change in instrument response characteristics between multipoint calibrations.		$ 40	$ 40
A4. Perform a zero and span calibration every 8 hours	Perform zero and span calibration every 8 hours as opposed to every 24 hours.	Reduces error due to the nonlinear component of zero drift.	$100	500	600
A5. Sample Diffusion Chamber	Place a diffusion chamber in the sample inlet line with sufficient capacity to integrate or smooth out peak concentrations of less than 5 minutes duration.	Reduces reading error by eliminating sharp spikes from the strip chart trace.	1	10	11
A6. Temperature Control	Install heating/cooling system capable of maintaining ambient room temperature to within $\pm$ 5°F (3°C) of a preset value.	Reduces zero drift caused by voltage variations and noise spikes resulting from sudden voltage changes.	55	20	75

Table 6: Quality Control Procedures or Actions (Concl'd)

Procedure	Description of Action	Expected Results	Costs		
			Equip	Personnel	Total
A7. Voltage Control	Install constant voltage regulator capable of maintaining line voltage to within ± 1% of a preset value.	Reduces zero drift caused by voltage variations and noise spikes resulting from sudden voltage changes.	$ 15	None	$ 15
A8. Improve water vapor interference control	Improve water vapor interference control by equipment change and/or increased maintenance.	Maintains water vapor interference to a insignificant level when compared to normal measurement error.	25	$ 10	35

of the Management Manual by setting

$$\hat{\tau} = \bar{d}_1 + \bar{d}_2 + \bar{d}_3$$

and

$$\hat{\sigma}_T = \sqrt{s_1^2 + s_2^2 + s_3^2}$$

If the relationship of (1) above is satisfied, no control procedures are required.

3) If the desired performance standard is not satisfied, identify the major error components.

4) Select the quality control procedure(s) which will give the desired improvement in data quality at the lowest cost. Figure 18 in Section 4.3 of the Management Manual illustrates a method for accomplishing this.

The relative position of actions on the graph in Figure 18 will differ for different monitoring networks according to type of equipment being used, available personnel, and local costs. Therefore, each network would need to develop its own graph to aid in selecting the control procedure providing the desired data quality at the lowest cost.

3.5 Procedures for Changing the Auditing Level to Give the Desired Level of Confidence in the Reported Data

The auditing process does not in itself change the quality of the reported data. It does provide a means of assessing the data quality. An increased auditing level increases the confidence in the assessment. It also increases the overall cost of data collection.

Various auditing schemes and levels are discussed in Section 4.2. Numerous parameters must be known or assumed in order to arrive at an optimum auditing level. Therefore, only two decision rules with two levels of auditing each will be discussed here.

For conditions as assumed in C of Section 4.2 of the Management Manual, a study of Figure 17 gives the following results. These conditions may or may not apply to your operation. They are included here to call attention to a methodology. Local costs must be used for conditions to apply to your operation.

A. Decision Rule - Accept the Lot as Good If No Defects Are Found (i.e., d = 0).

1) Most Cost Effective Auditing Level - In Figure 17 the two solid lines are applicable to this decision rule, i.e., d = 0. The cost curve has a minimum at n = 7 or an auditing level of 7 checks out of 100 sampling periods. From the probability curve it is seen that at this auditing level there is a probability of 0.47 of accepting a lot as good when the lot (for N = 100) actually has 10 defects with an associated average cost of 234 dollars per lot.

2) Auditing Level for Low Probability of Accepting Bad Data - Increasing the auditing level to n = 20, using the same curves in Figure 17 as in (1) above, shows a probability of 0.09 of accepting a lot as good when the lot actually has 10 defects. The average cost associated with this level of auditing is approximately 430 dollars per lot.

B. Decision Rule - Accept the Lot as Good If No More Than One (1) Defect is Found (i.e., $d \leq 1$).

1) Most Cost Effective Auditing Level - From the two dashed curves in Figure 17 it can be seen that the cost curve has a minimum at n = 14. At this level of auditing there is a probability of 0.51 of accepting a lot of data as good when it has 10 defects. The average cost per lot is approximately 340 dollars.

2) Auditing Level for Low Probability of Accepting Bad Data - For an auditing level of n = 20 the probability of accepting a lot with 10 percent defects is about 0.36 as read from the $d \leq 1$ probability curve. The average cost per lot is approximately 375 dollars.

It must be realized that the shape of a cost curve is determined by the assumed costs of performing the audit and of reporting bad data. These costs must be determined for individual monitoring situations in order to select optimum auditing levels.

3.6 Monitoring Strategies and Cost

Selecting the optimum monitoring strategy in terms of cost and data quality requires a knowledge of the present data quality, major error components, cost of implementing available control procedures, and potential increase in system precision and accuracy.

Section 4.3 illustrates a methodology for comparing strategies to obtain the desired precision of the data. Table 6 of Section 3.4 lists control procedures with estimated costs of implementation and expected results in terms of which error component(s) are affected by the control.

Three system configurations identified as best strategies in Figure 18, Section 4.3 of the Management Manual are summarized here.

A. Reference Method

Description of Method: This refers to a sampling system as illustrated in Figure 2, Section 2.2 of the Operations Manual. Routine operating procedures as given in the Operations Manual are to be followed with special checks performed to identify problem areas when performance standards are not being met. An auditing level of n = 7 out of a lot size of N = 100 is recommended for this strategy. This strategy is identified as A0 in Table 13 and Figure 18 in the Management Manual.

Costs: Taken as reference or zero cost.

Data Quality: Combining the assumptions made concerning water vapor interference and data processing errors with the standard deviation of measuring control samples (Ref. 1), the data quality is described by

$$C_t = C_m - (0.025\ C_t + 0.30) \pm 3(0.93)\ .$$

For a true concentration, C_t, of 10 ppm the measured value, C_m, will be within the following limits

$$7.8 < C_m < 13.3$$

approximately 99.7 percent of the time.

B. Reference Method with Sample Diffusion Chamber (A5)

Description of Method: Identical with (A) above except a diffusion chamber large enough to integrate or smooth out sharp spikes of less than 5 minutes duration is used. This reduces the chance of large errors in what can be a highly subjective process in the measurement method.

Costs: Estimated average cost per lot in excess of the costs of (A) above is 10 dollars.

Data Quality: From Table 13 and Figure 18 the data quality would be described by

$$C_t = C_m - (0.025\ C_t + 0.3) \pm 3(0.82).$$

For a true concentration, C_t, of 10 ppm the measured value, C_m, would fall within the following limits

$$8.1 < C_m < 13.0$$

approximately 99.7 percent of the time.

C. Reference Method Plus Sample Diffusion Chamber (A5) and Shelter Temperature Control Unit (A6).

Description of Method: Identical to (B) above with the addition of operating the analyzer in a shelter where the temperature is controlled to within $\pm$ 5°F of a set value.

Costs: From Figure 18 it is seen that the average cost per lot of data in excess of the cost of (A) above is about 85 dollars.

Data Quality: The combination of A5 and A6 as shown in Figure 18 has a standard deviation of about 0.7 ppm. Neither A5 nor A6 affect system bias; therefore, data quality can be reported as

$$C_t = C_m - (0.025\ C_t + 0.30) \pm 3(0.7) \ .$$

For a true concentration, C_t, of 10 ppm the measured value, C_m, will fall within the following limits

$$8.5 < C_m < 12.7$$

approximately 99.7 percent of the time.

PART III. MANAGEMENT MANUAL

4.0 GENERAL

The objectives of a data quality assurance program for the NDIR method of measuring the atmospheric carbon monoxide were given in Section 1.0. In this section of the manual, procedures will be given to assist the manager in making decisions pertaining to data quality based on the checking and auditing procedures described in Sections 2 and 3. These procedures can be employed to:

1) detect when the data quality is inadequate,
2) assess overall data quality,
3) determine the extent of independent auditing to be performed,
4) relate costs of data quality assurance procedures to a measure of data quality, and to
5) select from the options available to the manager the alternative(s) which will enable him to meet the data quality goals by the most cost-effective means.

Objectives 1 and 2 above are described in Section 4.1. The determination of the extent of auditing is considered in Section 4.2. Finally the Objectives 4 and 5 are discussed in Section 4.3. The cost data are assumed and a methodology provided. When better cost data become available, improvements can be made in the management decisions.

If the current reference system is providing data quality consistent with that required by the user, there will be no need to alter the physical system or to increase the auditing level. In fact, several detailed procedures could be bypassed if continuing satisfactory data quality is implied by the audit. However, if the data quality is not adequate, i.e. either a large bias and/or imprecision in the reported data, then (1) increased auditing should be employed, (2) the assignable cause is to be determined, and (3) the system deficiency corrected. The correction can take the form of a change in the operating procedure, e.g. increased frequency of calibration, such as every month; or it may be

improved instrumentation to control environmental variations during the sampling period, i.e. between zero-span calibrations. Another possibility is to increase the auditing level and hence increase the confidence in the reported results. These alternatives will be considered in Section 4.2.

4.1 Data Quality Assessment

As a result of the audits suggested in the Supervision Manual, one can (1) compare the estimated variations in the measured concentrations with suggested standards, (2) make an overall data quality assessment, and (3) detect when the data quality may be inadequate. It is important that the audit procedure be independent of previously reported results and be a true check of the system under normal operating procedures. Independence can be achieved by providing a control sample of unknown concentration to the operator and requesting that he measure and report the concentration of the sample or having another person perform the check. To insure that the check is made under normal operating procedures, it is required that the audit be performed without any special check of the system prior to the audit other than that usually performed each sampling period, such as a zero and span calibration.

Assume for convenience that an auditing period consists of N = 100 days (or sampling periods). Subdivide the auditing period into n equal periods or nearly equal periods. Make one audit during each period and compute the deviations (differences) between the audit values and the stated values (or previously determined values as determined by the operator) as indicated in the Supervision Manual. For example, if seven audits (n = 7) are to be performed over 100 sampling periods (N = 100), the 100 periods can be subdivided into 7 intervals (6 with 14 periods and 1 with 16 periods). The audit scheme for the data processing errors will be slightly different from the above and will be discussed under 3) below. The checks are to be combined for the selected auditing period and the mean difference or bias and the standard deviation of the differences are to be computed as indicated below.

1) Measurement of Control Samples

$$\text{Bias} = \bar{d}_1 = \frac{\sum_{i=1}^{n} d_{1i}}{n}$$

where

d_{1i} = deviation of measured concentration of CO from the stated value for the control sample.

$$\text{Standard Deviation} = s_1 = \sqrt{\frac{\Sigma(d_{1i} - \bar{d}_1)^2}{n-1}} \ ,$$

where

$\bar{d}_1$ - the average bias, and

s_1 = the estimated standard deviation of the measured concentrations corrected for the average bias $\bar{d}_1$.

The level of sampling or auditing n will be considered as a parameter to to be selected by the manager to maintain the quality of data as required.

2) Error Due to Water Vapor Interference

$$\text{Bias} = \bar{d}_2 = \frac{\sum_{i=1}^{n} d_{2i}}{n} \ ,$$

where

d_{2i} = deviation of the measured concentrations under saturated and dry conditions.

$$\text{Standard Deviation} = s_2 = \sqrt{\frac{\sum_{i=1}^{n} (d_{2i} - \bar{d}_2)^2}{n-1}} \ .$$

The formulas for average bias and the estimated standard deviations are the standard ones given in statistical texts (e.g., see Ref. 7).

3) Errors in Data Reduction and Recording

An auditing procedure for data processing errors was described in the Supervision Manual, Section 3.1. This procedure suggested that two hours be selected at random during each sampling period, that an independent check of the concentration of CO be obtained for these hours, and the differences between the hourly averages obtained by the operator, C_{oi}, and the corresponding check values, C_{ci}, i.e., $C_{oi} - C_{ci}$, be computed. These differences are treated as a go/no-go check, i.e., if either one of the differences is larger than $\pm$ 1 ppm, all hourly averages for that period (day) are rechecked and corrected; otherwise, no corrections are made. The value $\pm$ 1 ppm is a suggestion only; experience or results from the auditing process will indicate a more appropriate limit to use.

In order to compute an overall bias and standard deviation associated with the data processing, request that the values of d_{3i} be reported with the data (see Section 3.1.B in the Supervision Manual) and calculate

$$\text{Bias} = \bar{d}_3 = \frac{\sum_{i=1}^{n} d_{3i}}{n} \text{, and}$$

$$\text{Standard Deviation} = s_3 = \sqrt{\frac{\sum_{i=1}^{n} (d_{3i} - \bar{d}_3)^2}{n-1}} \text{ .}$$

A. Assessment of Data Quality

The above values completely describe the variation of the reported data from the true or stated concentrations in that all the operator, instrument, environmental, and data reduction errors are contained as components of one of the three errors. Hence, an overall statement of data quality can be obtained by combining these results as follows:

$$\text{Overall Bias } \hat{\tau} = \bar{d}_1 + \bar{d}_2 + \bar{d}_3$$

where the individual biases are set equal to zero if they are negligible or not significantly different from zero.

$$\text{Overall Standard Deviation} = \hat{\sigma}_T = \sqrt{s_1^2 + s_2^2 + s_3^2} ,$$

and hence the true concentration should fall in the following interval where C_m is the measured concentration,

$$C_m - \hat{\tau} \pm 2\hat{\sigma}_T{}^*,$$

approximately 95 percent of the time, or within the interval

$$C_m - \hat{\tau} \pm 3\hat{\sigma}_T$$

approximately 99.7 percent of the time. The value $2\hat{\sigma}_T$ is actually dependent on the number of audits conducted. If n is large, say about 25 or larger, the value 2 is appropriate.

In reporting the data quality, the bias, overall standard deviation, and auditing level should be reported in an ideal situation. (See Section 4.4 for further discussion on data presentation.) More restricted information is suggested in the Supervision Manual as a minimal reporting procedure.

In summary, the data provided by these three audits is sufficient to provide an overall estimate of the data quality. One assumption has been made in this analysis, which can be checked with the accumulation of data, i.e., the values of s_1, s_2, and s_3 have been assumed to be independent of the concentration level. In practice a slight dependence on the concentration level is expected, and thus the data should be logically grouped to measure the variation at low, intermediate, and high concentration levels within the range of concentrations normally measured.

If the overall reported precisions/biases of the data meet or satisfy the requirements of the user of the data, then a reduced auditing level may be employed; on the other hand, if the data quality is not

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*A positive bias in the measurement must be subtracted from the measured value when estimating the true concentration.

adequate, assignable causes of large deviations should be determined, and appropriate action taken to correct the deficiencies. This determination may require an increased checking or auditing of the measurement process as well as the performance of certain quality control checks, e.g., monitor temperature and voltage variations over 24-hour sampling period, check zero and span calibration procedures, determine adequacy of calibration curve, etc.

B. Assessment of Individual Measurements

Individual checks on the standard deviations of the three audits can be made by computing the ratio of the estimated standard deviation, s_i, to the corresponding suggested standard, σ_i, given in Table 7. If this ratio exceeds values given in Table 7 for any one of the audits, this would indicate that the source of trouble may be assigned to that particular aspect of the measurement process. Critical values of this ratio are given in Figure 13 as a function of sample size and two levels of confidence. Having assessed the general problem area, one then needs to perform the appropriate quality control checks to determine the specific causes of the large deviations.

4.2 Auditing Schemes

Auditing a measurement process costs time and money. On the other hand, reporting poor quality data also can be very costly. For example, the reported data might be used to determine a relationship between health damage and concentrations of certain pollutants. If poor quality data are reported, it is possible that invalid inferences or standards derived from the data will cost many dollars. These implications may be unknown to the manager until some report is provided to him referencing his data; hence, the importance of reporting the precision and bias with the data.

Table 7 : Critical Values of s_i/σ_i

Level of Confidence	Statistic	n=5	n=10	n=15	n=20	n=25
90%	s_i/σ_i	1.40	1.29	1.23	1.20	1.18
95%	s_i/σ_i	1.54	1.37	1.30	1.26	1.23

s_i = estimated standard deviation

σ_i = hypothesized or suggested standard deviation

Audit	Suggested Standard
Control Sample	σ_1 = 0.72 (at 10 ppm)
Water Vapor	σ_2 = 0.30
Data Reduction	σ_3 = 0.50
Overall Standard Deviation	σ_T = 0.93 (at 10 ppm)*

*For concentrations different from 10 ppm, use $\sigma_1 = 0.072$ (concentration in ppm), and

$$\sigma_T^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2,$$

until further information concerning the dependence of σ_1 on the concentration of CO is obtained.

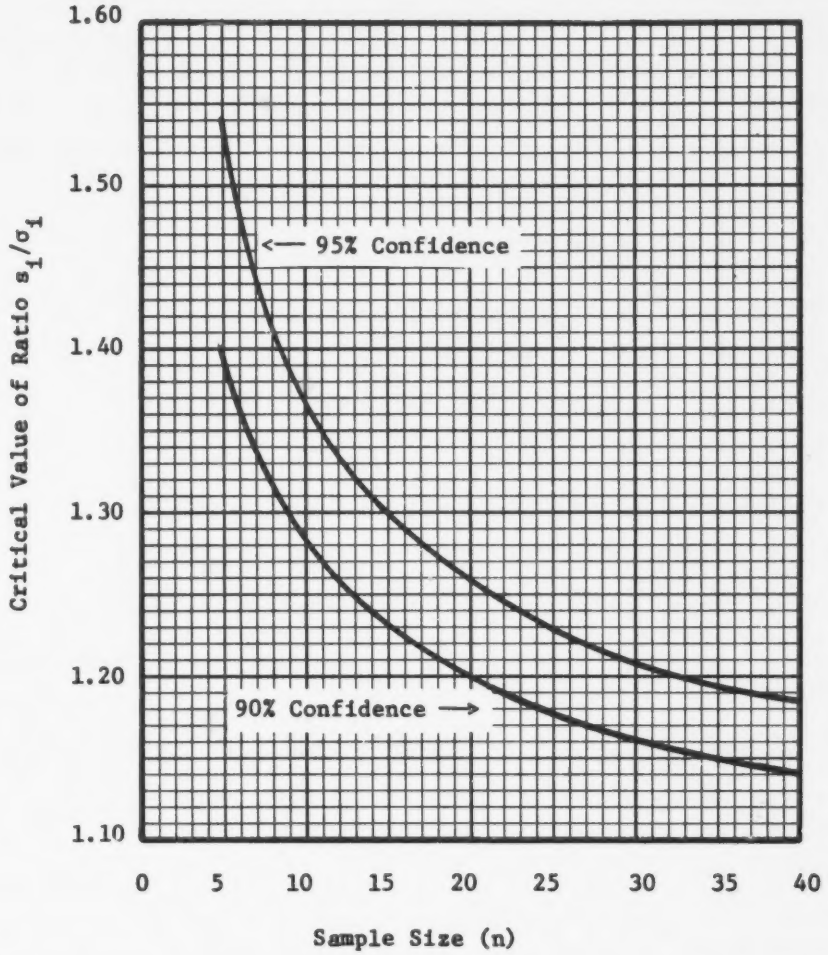

Figure 13: Critical Values of Ratio s_i/σ_i Vs. n

As a result of the cost of reporting poor quality data, it is desirable to perform the necessary audits to assess the data quality and to invalidate unsatisfactory data with high probability. On the other hand, if the data quality is satisfactory, an auditing scheme will only increase the data measurement and processing cost. An appropriate tradeoff or balance of these costs must be sought. These costs are discussed in Section C below.

Consider the use of a control sample to check the major errors in the NDIR measurement process. Using the suggested standard deviation of 0.72 ppm for the measured concentration of CO at about the 10 ppm level and a range of 1% in the deviation of the stated concentration of the control sample from the true concentration, a single measured concentration should fall between $10 \pm 0.1 \pm 2(0.72)$ppm or 10 ± 1.54 ppm approximately 95% of the time, $10 \pm 0.1 \pm 3(0.72)$ppm or 10 ± 2.26 ppm approximately 99.7% of the time. A deviation outside the 2σ (or 3σ) limits is considered a defect in enforcement (or routine) monitoring of air quality. The number of defects can be determined from the results of the reported audits.

Now consider the implication of an auditing scheme to determine or judge the quality of the reported data in terms of an acceptance sampling scheme. Let the data be assembled into homogeneous lots of N = 50 or 100 sampling periods. Suppose that n = 7 (10, 15, or 20) periods are sampled in the manner suggested in Section 3.1. That is, one day is selected at random during each 14 periods, and for 100 periods a sample of size 7 would be obtained. Figure 14 gives a diagram of the data flow, sampling, and decision making process.

A. Statistics of Various Auditing Schemes

Suppose that the lot size is N = 100 periods (days), that n = 7 periods are selected at random, and that there are 5% defectives in the 100, or 5 defectives. The probability that the sample of 7 contains 0, 1, ..., 6 defectives is given by the following.

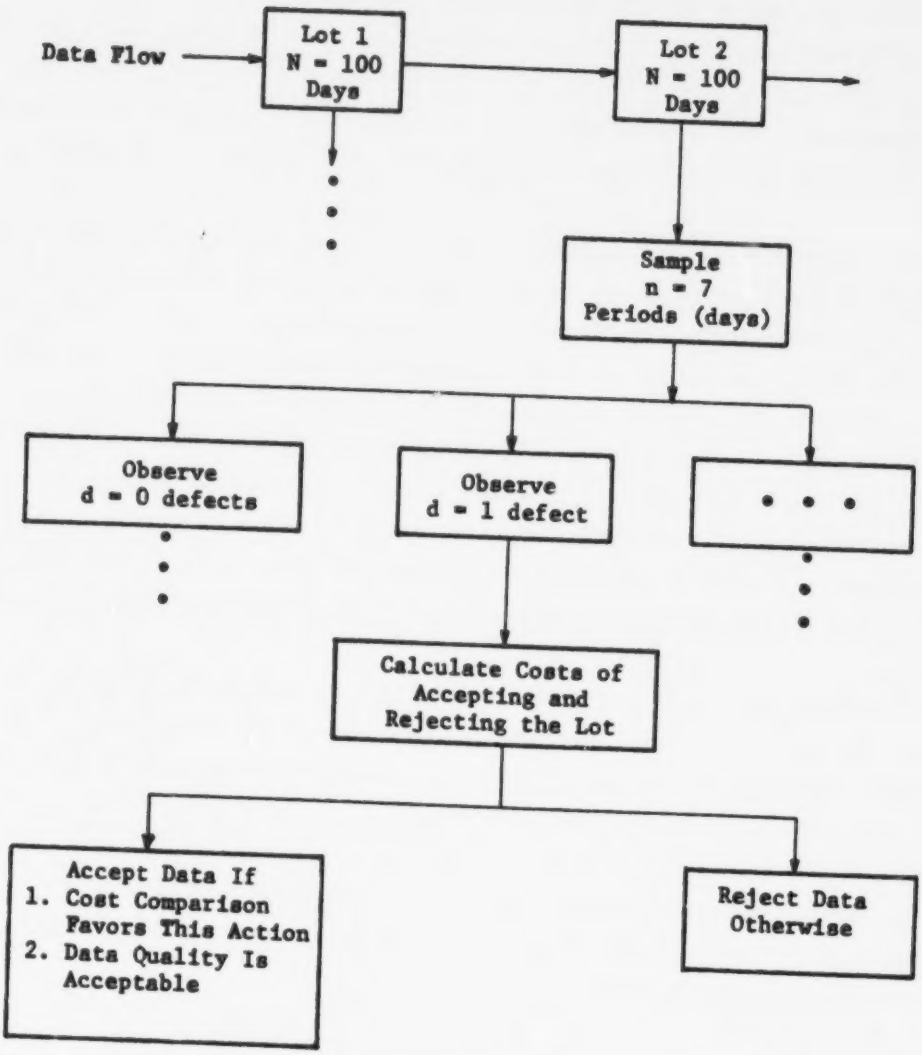

Figure 14: Data Flow Diagram for Auditing Scheme

$$p(0 \text{ defectives}) = \frac{\binom{5}{0}\binom{95}{7}}{\binom{100}{7}}^{*},$$

and for d defectives

$$p(d \text{ defectives}) = \frac{\binom{5}{d}\binom{95}{7-d}}{\binom{100}{7}}, \quad d \leq 5 .$$

The values are tabulated below for d = 0, 1, ..., 6 and for the two data quality levels.

	Data quality	
d	D=5% Defectives	D=15% Defectives
0	0.6903	0.3083
1	0.2715	0.4098
2	0.0362	0.2152
3	0.0020	0.0576
5	0.00004	0.0084
6	= 0	≈0

Figure 15A gives the probabilities of d = 0 and d ≤ 1 defectives as a function of sample size. The probability is given for lot size N = 100, D = 5 and 15% defectives, for sample sizes (auditing levels) from 1 to 20. For example, if n = 10 measurements are audited and D = 5% defectives, the probability of d=0 defectives is 0.58. Figure 15B gives the probabilities for lot size N = 50, for D = 6, 10, and 20% defectives, and for d = 0 and d ≤ 1. These curves will be used in calculating the cost relationships of Section C.

* $\dfrac{\binom{5}{0}\binom{95}{7}}{\binom{100}{7}} = \dfrac{\left(\frac{5!}{0!5!}\right)\left(\frac{95!}{7!88!}\right)}{\left(\frac{100!}{7!93!}\right)} = \dfrac{95 \cdot 94 \cdots 89}{100 \cdot 99 \cdots 94} = 0.6903.$

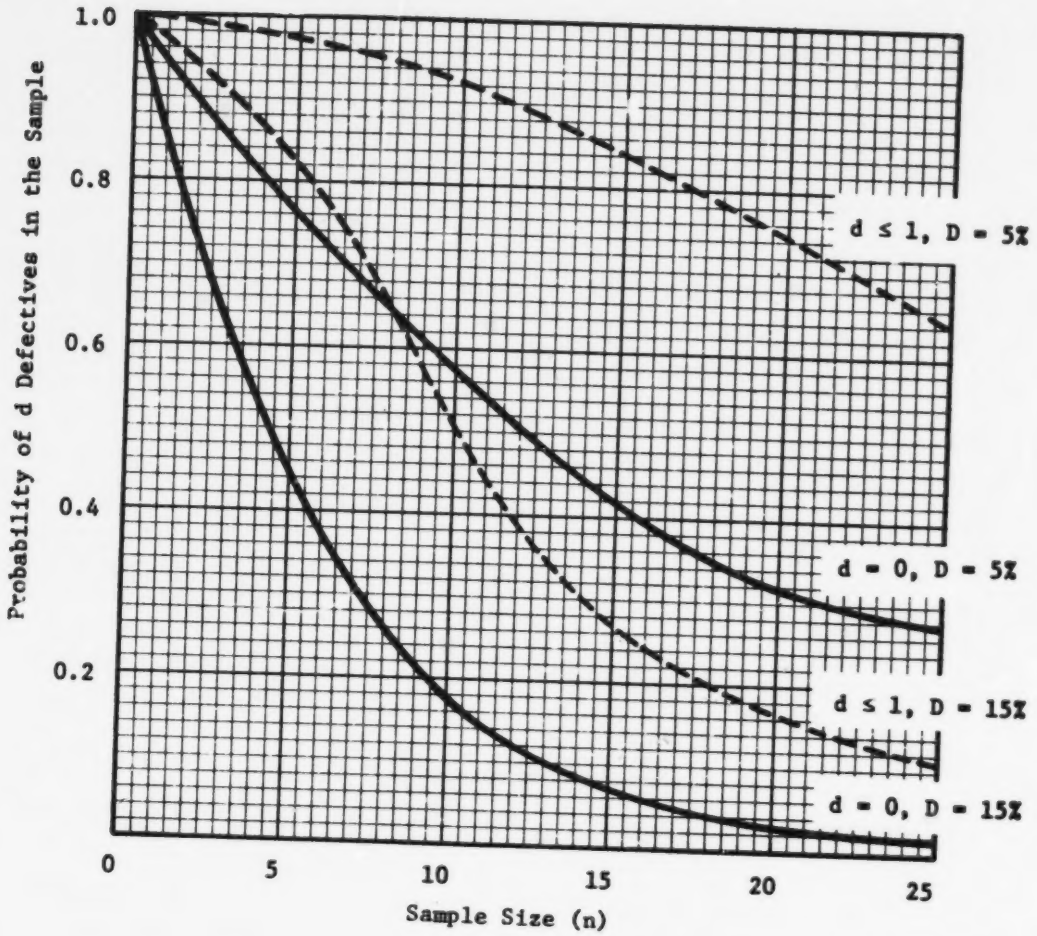

Figure 15A: Probability of d Defectives in the Sample If the Lot (N = 100) Contains D% Defectives

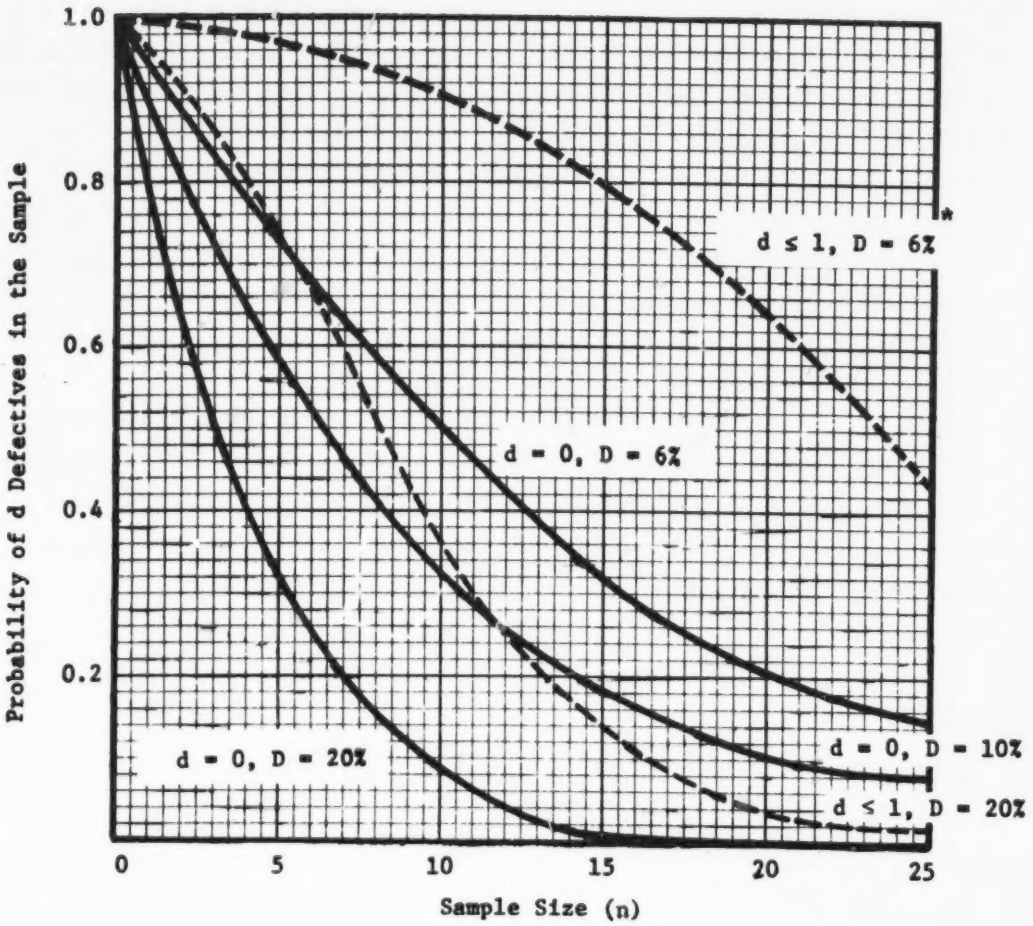

Figure 15B: Probability of d Defectives in the Sample If the Lot (N = 50) Contains D% Defectives.

*This graph is for a lot size of N = 50. Only whole numbers of defectives are physically possible; therefore, even values of D (i.e., 6, 10, and 20 percent) are given rather than the odd values of 5 and 15 percent as given in Figure 18A.

B. Selecting the Auditing Level

One consideration in determining an auditing level n used in assessing the data quality is to calculate the value of n which for a prescribed level of confidence will imply that the percent of defectives in the lot is less than ten percent, say, if zero defectives are observed in the sample.* Figures 16A and 16B give the percentage of good measurements in the lot sampled for several levels of confidence, 50, 60, 80, 90, and 95%. The curves in 16A assume that 0 defectives are observed in the sample, and 16B, 1 defective observed in the sample. The solid curves on the figures are based on a lot size of N = 100; two dashed curves are shown in Figure 16A for N = 50; the differences between the corresponding curves are small for the range of sample sizes considered.

For example, for zero defectives in a sample of 7 from a lot of N = 100, one is 50% confident that there are less than 10% defective measurements among the 100 reported values. For zero defectives in a sample of 15 from N = 100, one is 80% confident that there are less than 10% defective measurements. Several such values were obtained from Figure 16A and placed in Table 8 below for convenient reference.

Table 8: Required Auditing Levels n
for Lot Size N = 100
Assuming Zero Defectives

Confidence Level	D = 10%	15%	20%
50%	7	<5	<5
60%	9	6	<5
80%	15	10	8
90%	20	15	11
95%	≈ 25	18	13

*Obviously, the definition of defective need not always be the same and must be clearly stated each time. The definitions employed herein are based on results of collaborative test programs.

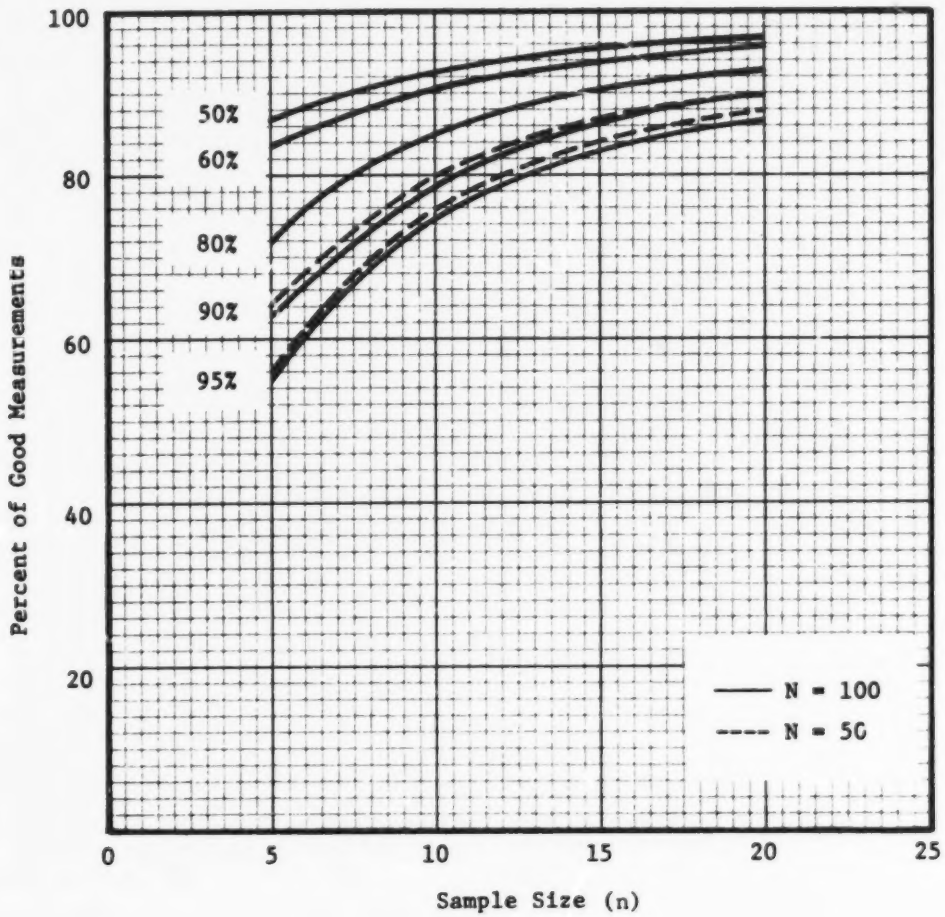

Figure 16A: Percentage of Good Measurements Vs. Sample Size for No Defectives and Indicated Confidence Level

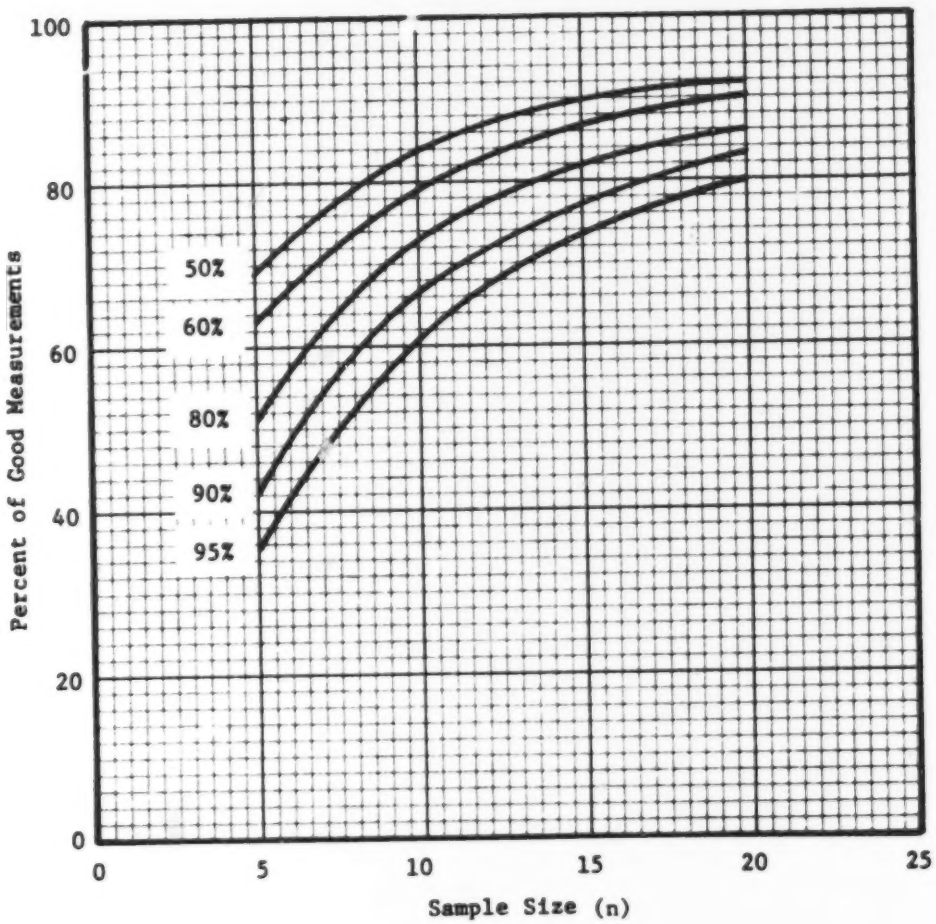

Figure 16B: Percentage of Good Measurements Vs. Sample Size for 1 Defective Observed and Indicated Confidence Level

Lot Size = 100

C. Cost Relationships

The auditing scheme can be translated into costs using the costs of auditing, rejecting good data, and accepting poor quality data. These costs may be very different in different geographic locations. Therefore, purely for purposes of illustrating a method, the cost of auditing is assumed to be directly proportional to the auditing level. For n = 7 it is assumed to be \$155 per lot of 100. The cost of rejecting good quality data is assumed to be \$600 for a lot of N = 100. The cost of reporting poor quality data is taken to be \$800. To repeat, these costs given in Table 9 are assumed for the purpose of illustrating a methodology of relating auditing costs to data quality. Meaningful results can only be obtained by using correct local information.

Table 9: Costs vs. Data Quality

	Data Quality	
	"Good" $D \leq 10\%$ Incorrect Decision	"Bad" $D > 10\%$ Correct Decision
Reject Lot of Data	Lose cost of performing* audit plus cost of rejecting good quality data. (-\$600 - \$155)	Lose cost of performing audit, save cost of not permitting poor quality data to be reported. (\$400 - \$155)
	Correct Decision	Incorrect Decision
Accept Lot of Data	Lose cost of performing audit. (-\$155)	Lose cost of performing audit plus cost of declaring poor quality data valid. (-\$800 - \$155)

*Cost of performing audit varies with the sample size; is assumed to be \$155 for n = 7 audits per N = 100 lot size.

Suppose that 50 percent of the lots have more than 10 percent defective and 50 percent have less than 10 percent defective. (The percentage of defective lots can be varied as will be described in the final report.) For simplicity of calculation, it is further assumed that the good lots have exactly 5 percent defectives and the poor quality lots have 15 percent defective.

Suppose that n = 7 measurements out of a lot N = 100 have been audited and none found to be defective. Furthermore, consider the two possible decisions of rejecting the lot and accepting the lot and the relative costs of each. These results are given in Tables 10A and 10B.

Table 10A: Costs If 0 Defectives are Observed and the Lot is Rejected

		Correct Decision	Incorrect Decision	Net Value ($)
Reject Lot	D = 5%	--- ---	$P_1 = 0.69$ $C_1 = -600 - 155$	$P_1C_1 = -\$521$
	D = 15%	$P_2 = 0.31$ $C_2 = 400 - 155$	---	$P_2C_2 = \$76$

Cost = $P_1C_1 + P_2C_2 = -\$445$

Table 10B: Costs If 0 Defectives are Observed and the Lot is Accepted

		Correct Decision	Incorrect Decision	Net Value ($)
Accept Lot	D = 5%	$P_1 = 0.69$ $C_3 = -155$	--- ---	$P_1C_3 = -\$107$
	D = 15%	---	$P_2 = 0.31$ $C_4 = -800 - 155$	$P_2C_4 = -\$296$

Cost = $P_1C_3 + P_2C_4 = -\$403$

The value $p_1(p_2)$ in the above table is the probability that the lot is 5% (15%) defective given that 0 defectives have been observed. For example,

$$p_1 = \frac{\left(\begin{array}{c}\text{probability that the lot is 5\% defective} \\ \text{and 0 defectives are observed}\end{array}\right)}{p\left(\begin{array}{c}\text{lot is 5\% defective and} \\ \text{0 defectives observed}\end{array}\right) + p\left(\begin{array}{c}\text{lot is 15\% defective and} \\ \text{0 defectives observed}\end{array}\right)}$$

$$= \frac{0.5(0.69)}{0.5(0.69) + 0.5(0.31)} = 0.69.$$

$$p_2 = \frac{\left(\begin{array}{c}\text{probability that the lot is 15\% defective} \\ \text{and 0 defectives are observed}\end{array}\right)}{p\left(\begin{array}{c}\text{lot is 5\% defective and} \\ \text{0 defectives observed}\end{array}\right) + p\left(\begin{array}{c}\text{lot is 15\% defective and} \\ \text{0 defectives observed}\end{array}\right)}$$

$$= \frac{0.5(0.31)}{0.5(0.31) + 0.5(0.69)} = 0.31.$$

It was assumed that the probability that the lot is 5% defective is 0.5. The probability of observing zero defectives, given the lot quality is 5% or 15%, can be read from the graphs of Figures 15A or 15B.

A similar table can be constructed for 1, 2, ..., defectives and the net costs determined. The net costs are tabulated in Table 11 for 1, 2, and 3 defectives. The resulting costs indicate that the decision preferred from a purely monetary viewpoint is to accept the lot if 0 defectives are observed and to reject it otherwise. The decision cannot be made on this basis alone. The details of the audit scheme also affect the confidence which can be placed in the data qualification; consideration must be given to that aspect as well as to cost.

Table 11: Costs in Dollars

Decision	d = number of defectives			
	0	1	2	3
Reject Lot	-445	-155	+101	+207
Accept Lot	-403	-635	-839	-928

D. Cost Vs. Audit Level

After the decision criteria have been selected, an average cost can be calculated. Based on the results of Table 11, the decision criterion is to accept the lot if d = 0 defectives are observed and to reject the lot if d = 1 or more defectives are observed. All the assumptions of the previous section are retained. The auditing level is later varied to obtain the data in Figure 17.

One example calculation is given below and summarized in Table 12. The four cells of Table 12 consider all the possible situations which can occur, i.e., the lots may be bad or good and the decision can be to either accept or reject the lot based on the rule indicated by Table The costs are exactly as indicated in Tables 10A and 10B. The probabilities are computed as follows.

q_1 = (prob. that the lot is 5% defective and 1 or more defects are obtained in the sample)

= (prob. that the lot is 5% defective)(prob. 1 or more defectives are obtained in the sample given the lot is 5% defective)

= 0.5 (0.31) = 0.155

Similarly q_2, q_3, and q_4 in Table 12 are obtained as indicated below.

$$q_2 = 0.5\ (0.69) = 0.345$$

$$q_3 = 0.5\ (0.69) = 0.345$$

$$q_4 = 0.5\ (0.31) = 0.155$$

The sum of all the q's must be unity as all possibilities are considered. The value 0.5 in each equation is the assumed proportion of good lots (or poor quality lots). The values 0.31 and 0.69 are the conditional probabilities that given the quality of the lot, either d = 0 or d = 1 or more defectives are observed in the sample. Further details of the computation are given in the final report of this contract.

Table 12: Overall Average Costs for One Acceptance - Rejection Scheme

Decision	Good Lots D = 5%	Bad Lots D = 15%	
Reject any lot of data if 1 or more defects are found.	$q_1 = 0.155$ $C_1 = -\$755$	$q_2 = 0.345$ $C_2 = \$245$	$q_1C_1 + q_2C_2 = -\$ 32$
Accept any lot of data if 0 defects are found.	$q_3 = 0.345$ $C_3 = -\$155$	$q_4 = 0.155$ $C_4 = -\$955$	$q_3C_3 + q_4C_4 = -\$202$

Average Cost = -$234

In order to interpret the concept of average cost, consider a large number of data lots coming through the system; a decision will be made on each lot in accordance with the above and a resulting cost of the decision will be determined. For a given lot, the cost may be any one of the four costs, and the proportion of lots with each cost is given by the q's. Hence the overall average cost is given by the sum of the product of q's by the corresponding C's.

In order that one may relate the average cost as given in Table 12 to the costs given in Table 11, it is necessary to weight the costs in Table 11 by the relative frequency of occurrence of each observed number of defectives, i.e., prob(d). This calculation is made below.

No. of Defectives	Decision Rule	Costs ($) from Table 11	Prob(d)	Cost × Prob(d)
d = 0	Accept	- 403	0.50	-$201.5
1	Reject	- 155	0.34	- 52.7
2	Reject	101	0.1255	12.6
3	Reject	207	0.030	6.2
4	Reject	244	0.0042	1.0
		Totals	0.9997	-$234.4

Thus the value -$234 is the average cost of Table 12 and the weighted average of the costs of Table 11. The weights, Prob(d), are obtained as follows:

$$\text{Prob}(d=0) = \text{Prob}(\text{lot is good } \underline{\text{and}}\ d=0 \text{ defectives are observed}) + \text{Prob}(\text{lot is poor quality } \underline{\text{and}}\ d=0 \text{ defectives are observed})$$

$$= 0.5\ (0.69) + 0.5\ (0.31) = 0.50.$$

This is the proportion of all lots which will have exactly 0 defectives under the assumptions stated. For d = 1, 2, 3, and 4 the values of the probabilities in parentheses above can be read from the table on page 87.

Based on the stated assumptions, the average cost was determined for several auditing levels as indicated in Table 12. These costs are given in Figure 17. One observes from this figure that n = 7 is cost effective given that one accepts the lot only if zero defectives are observed. (See curve for d = 0.

If the lots are accepted if either 0 or 1 defectives are observed, then referring to the curve $d \leq 1$, the best sampling level is n = 15. The curve of probability of d = 0 ($d \leq 1$) defectives in a lot of N = 100 measurements if there are 10% defectives is also given on the same figure.

Another alternative is to accept all data without performing an audit. Assuming that one-half (50%) of the lots contain more than 10% defectives, the average cost on a per lot basis would be 0.5(-$800) = -$400. This, however, would preclude qualification of the data. Regardless of cost it would be an unacceptable alternative.

4.3 Data Quality Versus Cost of Implementing Actions

The discussion and methodology given in the previous section was concerned with the auditing scheme (i.e., level of audit or sample size, costs associated with the data quality, etc.). Increasing the level of audit of the measurement process does not by itself change the quality of the data but it does increase the information about the

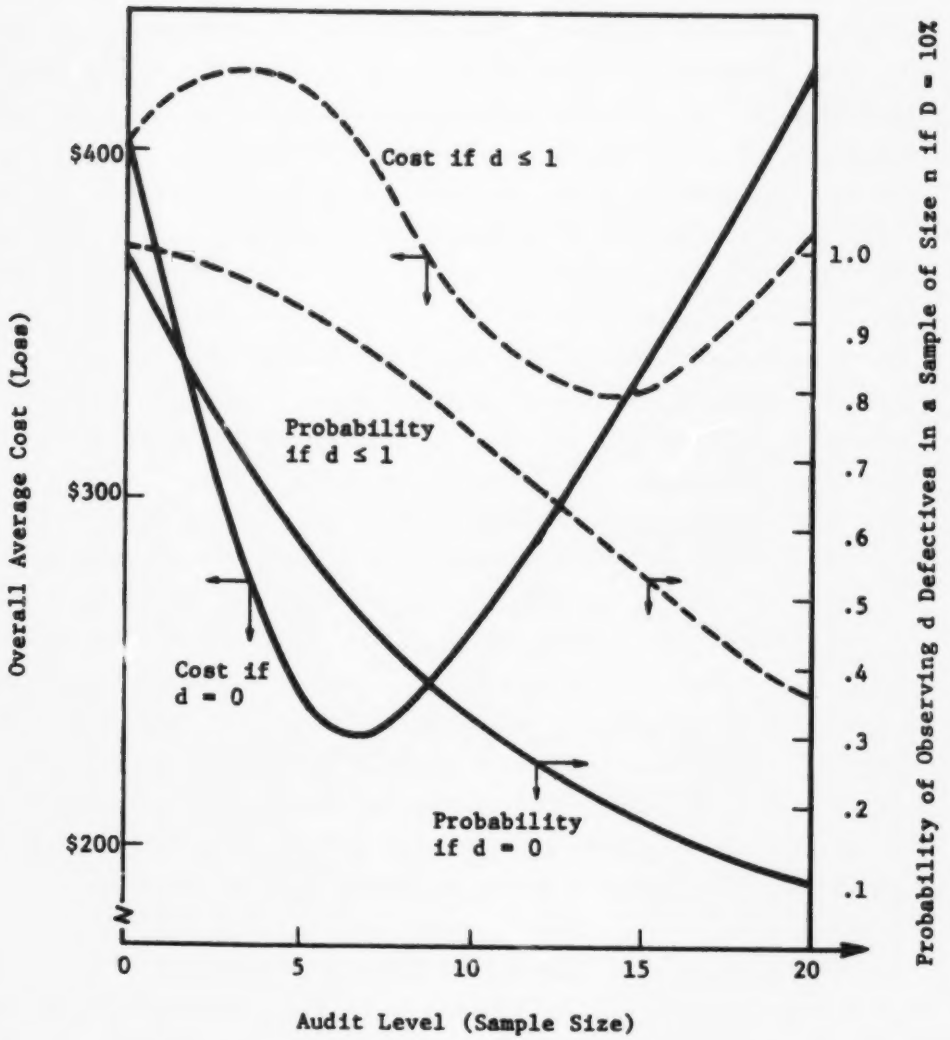

Figure 17: Average Cost Vs. Audit Level
(Lot Size N = 100)

quality of the reported data. Hence, fewer good lots will be rejected and more poor quality data will be rejected. If the results of the audit imply that certain process measurement variables are major contributors to the total error or variation in the reported concentration of CO, then alternative strategies for reducing these variations need to be investigated. This section illustrates a methodology for comparing the strategies to obtain the desired precision of the data. In practice it would be necessary to experiment with one or more strategies, determine the potential increase in precision, and relate the precisions to the relative costs as indicated herein. Several strategies are considered but only a few of the less costly ones would be acceptable as illustrated in Figure 18. The assumed values of the standard deviations and biases for each type audit are not based on actual data, except for the reference method. In this case values were taken from Ref. 1. These values are probably smaller than those experienced in the field.

Several alternative actions or strategies can be taken to increase the precision of the reported data. For example, if the instrument responses to voltage, temperature, and humidity variations are large contributors to the variation of an observed instrument response, then additional control equipment for one or more of the environmental effects can reduce the variation of the measured responses by calculated amounts and thus reduce the error of the reported concentrations. In this manner, the cost of the added controls can be related to the data quality as measured by the estimated errors of the reported results. It must be recognized that these errors are dependent to some extent on the concentration.

Suppose that it is desired to make a statement that the concentration of CO is within 2.1 ppm ($3\sigma_T$ limit) for 1 hour averages and that the minimal cost control equipment and checking procedures are to be employed to attain this desired precision. In order to determine a cost efficient procedure, it is necessary to estimate the variance for each source of error (or variation) for each strategy and then select the strategy or combination of strategies which yields the desired precision with minimum cost. One such calculation is summarized in Table 13 with assumed costs of equipment and control procedures.

Examining the graph in Figure 18 of cost versus precision, one observes that the combination of actions A5 and A6 is the least costly strategy that meets the required goal of 2.1 ppm ($\sigma_T \leq 0.7$ ppm) in the reported concentration. Similarly A5 meets the goal of 2.5 ppm ($\sigma_T \leq 0.83$ ppm). The assumed values of the standard deviations of the measured concentrations of CO for the alternative courses of action are given in Table 13. The estimated costs for the various alternatives are given in Table 6 of Section 3 and in Table 13.

Two curves are given in Figure 18 to illustrate the assumed relationship between cost of reporting poor quality data and the measure of precision σ_T. In one curve it is assumed that there is 0 cost in reporting data for which $\sigma_T \leq 0.60$ and the cost increases rapidly beyond $\sigma_T = 0.60$. The other curve assumes $\sigma_1 = 0.80$ is acceptable.

Data processing or data reduction errors have been included in these sample analyses for illustration purposes. The value assumed for σ_3 in Table 13 is an estimate and was not derived from actual data. If information regarding the distribution of data processing errors is desired, the field supervisor could be requested to forward actual values for d_{31}, d_{32}, ---, d_{37} with the data qualification form shown in Figure 12 of the Supervision Manual.

Table 13: Assumed Standard Deviations for Alternative Strategies

		Alternative Strategies*								
		A0	A1	A2	A3	A4	A5	A6	A7	A8
1. Control Sample	$\bar{d}_1$	0.25	0.25	0.25	0.10	0.25	0.25	0.25	0.25	0.25
	σ_1	0.72	0.70	0.69	0.68	0.54	0.72	0.57	0.68	0.72
2. Water Vapor Interference	$\bar{d}_2$	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.10
	σ_2	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.10
3. Data Reduction	$\bar{d}_3$	0	0	0	0	0	0	0	0	0
	σ_3	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
**σ_T^2 (overall variance)		0.86	0.83	1.82	0.80	0.63	0.67	0.66	0.80	0.78
**σ_T (overall std. dev.)		0.93	0.91	0.90	0.90	0.79	0.82	0.82	0.90	0.88
***Bias	Max. Pos.	0.55	0.55	0.55	0.40	0.55	0.55	0.55	0.55	0.35
	Max. Neg.	0	0	0	0	0	0	0	0	0
Added Cost/100 Periods		$0	$90	$40	$40	$600	$11	$75	$15	$35

*Alternative Strategies are given in Table 6, Section 3; the σ_i's, i=1, 2, and 3, are assumed values based on results given in Ref. 1, and where data are not available they are engineering judgments.

**$\sigma_T^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2$, $\sigma_T = \sqrt{\sigma_T^2}$.

***Bias = $\tau = \bar{d}_1 + \bar{d}_2 + \bar{d}_3$; the biases and standard deviations which are dependent on concentration level are determined at 10 ppm. In order to estimate the true concentration, the estimated bias τ must be subtracted from the measured concentration and then the appropriate $2\sigma_T$ or $3\sigma_T$ error added, i.e., $c_m - \tau \pm 2\sigma_T$, gives the 95% limits.

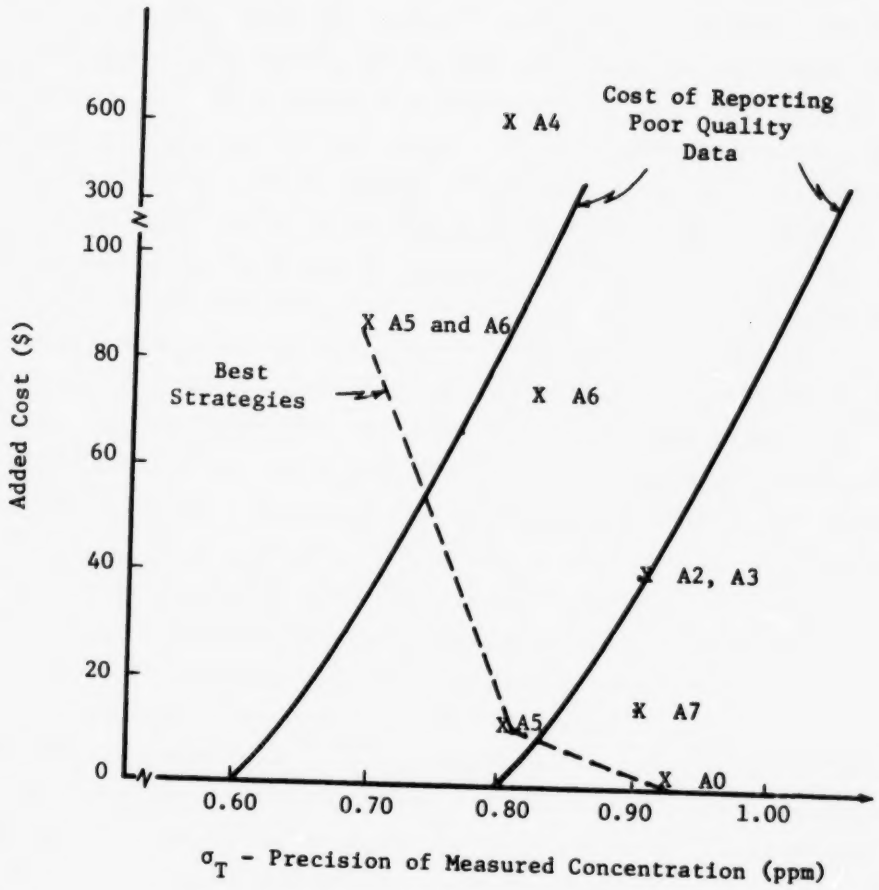

Figure 18: Costs Vs. Precision for Alternative Strategies

4.4 Data Presentation

A reported value whose precision and accuracy (bias) are unknown is of little, if any, worth. The actual error of a reported value—that is, the magnitude and sign of its deviation from the true value--is usually unknown. Limits to this error, however, can usually be inferred, with some risk of being incorrect, from the precision of the measurement process by which the reported value was obtained and from reasonable limits to the possible bias of the measurement process. The bias, or systematic error, of a measurement process is the magnitude and direction of its tendency to measure something other than what was intended; its precision refers to the closeness or dispersion of successive independent measurements generated by repeated applications of the process under specified conditions, and its accuracy is determined by the closeness to the true value characteristic of such measurements.

Precision and accuracy are inherent characteristics of the measurement process employed and not of the particular end result obtained. From experience with a particular measurement process and knowledge of its sensitivity to uncontrolled factors, one can often place reasonable bounds on its likely systematic error (bias). This has been done in the model for the measured concentration as indicated in Table 13. It is also necessary to know how well the particular value in hand is likely to agree with other values that the same measurement process might have provided in this instance or might yield on measurements of the same magnitude on another occasion. Such information is provided by the estimated standard deviation of the reported value, which measures (or is an index of) the characteristic disagreement of repeated determinations of the same quantity by the same method and thus serves to indicate the precision (strictly, the imprecision) of the reported value.

A reported result should be qualified by a quasi-absolute type of statement that places bounds on its systematic error and a separate statement of its standard deviation, or of an upper bound thereto, whenever a reliable determination of such value is available. Otherwise a computed value of the standard deviation should be given together with a statement of the number of degrees of freedom on which it is based.

As an example, consider the example given in Section 4.3, Table 13. In this case the estimated 2σ limits of the reported concentration of CO by the NDIR reference method are $\pm$ 2(0.93) or $\pm$ 1.86 ppm. Suppose that a positive bias of 0.3 ppm results from the water vapor interference, then the results could be reported as the measured concentration, C_m, with the following 2σ limits and audit level, e.g.,

$$C_m - 0.3 \pm 1.9 \text{ ppm}, \; n = 20 \; .$$

The replication error is a measure of the variation of successive determination of CO with the same operator and instrument on the same sample within a time interval short enough to avoid change of environmental factors. This replication error as given by the standard deviation s was measured to be about 0.17 mg/m^3 (.15 ppm).

The repeatability error is a measure of the variation between test results on the same sample on different days by the same laboratory. The standard deviation was estimated to be s = 0.57 mg/m^3 (.50 ppm). This measure of variation must by definition include the replication error, i.e.,

$$\sigma(\text{repeatability}) = [\sigma^2(\text{replication}) + \sigma^2 \text{ (day)}]^{1/2}.$$

It is indicated (Ref. 1) that the σ for repeatability varies significantly between laboratories; it appears to depend on the concentration but the results are erratic.

The requirements for reporting data quality as outlined in the Supervision Manual involves adopting a standard, performing an audit, and comparing the audit result to the standard. A defect is defined in terms of the standard. This approach does not make maximum use of the collected data, but its simplicity should aid in the implementation of a quality assurance program. After experience has been gained in using the auditing scheme and in calculating the results, it is recommended that the above, more comprehensive method of data presentation be implemented.

4.5 Personnel Requirements

Personnel requirements as described here are in terms of the NDIR method only. It is realized that these requirements may be only a minor factor in the overall requirements from a systems point of view where several measurement methods are of concern simultaneously.

A. Training and Experience

1. Director

The director or one of the professional-level employees should have a basic understanding of statistics as used in quality control. He should be able to perform calculations, such as the mean and standard deviation, required to define data quality. The importance of and requirements for performing independent and random checks as part of the auditing process must be understood. Three references which treat the above-mentioned topics are listed below:

Probability and Statistics for Engineers, Irvin Miller and John E. Freund, published by Prentice-Hall, Inc., Englewood, N. J., 1965.

Introductory Engineering Statistics, Irwin Guttman and S. S. Wilks, published by John Wiley and Sons, Inc., New York, N. Y., 1965.

The Analysis of Management Decisions, William T. Morris, published by Richard D. Irwin, Inc., Homewood, Illinois, 1964.

2. Operator

There are or can be two levels of operation involved in the NDIR method.

First, an operator or technician who is involved in the preliminary or initial setup and checkout or is responsible for troubleshooting and repairing the analyzer should have technical training in electronics and/or instrumentation as obtained in a technical or service school or

several years of on-the-job experience. For a specific analyzer it would be desirable to have the technician checked out by a manufacturer's representative or at least to have him participate, with the representative, in the initial installation and startup. The manufacturer's instruction book should be available for study or reference by the technician.

Routine operations involve the use of external controls only and require no high-level skills. A high school graduate with proper supervision and on-the-job training can become effective at this level in a very short time.

An effective on-the-job training program could be as follows:

a) Observe experienced operator perform the different tasks in the measurement process.

b) Study the operational manual of this document and use it as a guide for performing the operations.

c) Perform operations under the direct supervision of an experienced operator.

d) Perform operations independently but with a high level of quality control checks utilizing the technique described in the section on Operator Proficiency Evaluation Procedures below to encourage high quality work.

Another alternative would be to have the operator attend an appropriate basic training course sponsored by EPA.

4.6 Operator Proficiency Evaluation Procedures

One technique which may be useful for early training and qualification of operators is a system of rating the operators as indicated below.

Various types of violations (e.g., invalid sample resulting from operator carelessness, failure to maintain records, use of improper equipment, or calculation error) would be assigned a number of demerits depending upon the relative consequences of the violation. These demerits could then be summed over a fixed period of time of one week, month, etc., and a continuous record maintained. The mean and standard deviation of the number of demerits per week can be determined for each operator and

a quality control chart provided for maintaining a record of proficiency of each operator and whether any changes in this level have occurred. In comparing operators, it is necessary to assign demerits on a per unit work load basis in order that the inferences drawn from the chart be consistent. It is not necessary or desirable for the operator to be aware of this form of evaluation. The supervisor should use it as a means of determining when and what kind of instructions and/or training is needed.

A sample QC chart is given in Figure 19 below. This chart assumes that the mean and standard deviation of the number of demerits per week, e.g., are 5 and 1, respectively. After several operators have been evaluated for a few weeks, the limits can be checked to determine if they are both reasonable and effective in helping to improve and/or maintain the quality of the air quality measurement.

The limits should be based on the operators whose proficiency is average or slightly better than average. Deviations outside the QC limits, either above or below, should be considered in evaluating the operators. Identifying those operators whose proficiency may have improved is just as important as knowing those operators whose proficiency may have decreased.

The above procedure may be extended to an entire monitoring network (system). With appropriate definitions of work load, a continuous record may be maintained of demerits assigned to the system. This procedure might serve as an incentive for teamwork, making suggestions for improved operation procedures, etc.

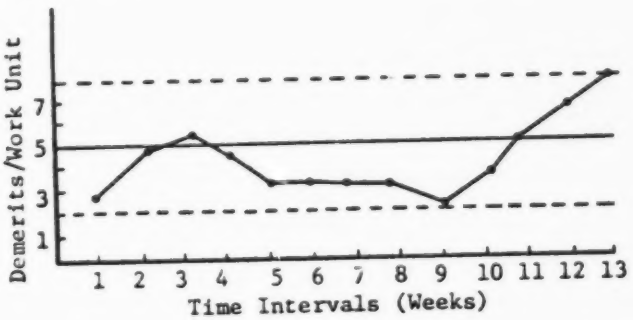

Figure 19: Sample QC Chart for Evaluating Operator Proficiency

REFERENCES

1. Herbert C. McKee et al., "Collaborative Study of Reference Method for the Continuous Measurement of Carbon Monoxide in the Atmosphere (Non-Dispersive Infrared Spectrometry)," Southwest Research Institute, Contract CPA 70-40, SwRI Project 01-2811, San Antonio, Texas, May 1972.

2. Frank McElroy, "The Intech NDIR-CO Analyzer," presented at the 11th Methods Conference in Air Pollution, University of California Berkeley, California, April 1, 1970.

3. Hezekiah Moore, "A Critical Evaluation of the Analysis of Carbon Monoxide with Nondispersive Infrared (NDIR)," presented at the 9th Conference on Methods in Air Pollution and Industrial Hygiene Studies, Pasadena, California, February 7-9, 1968.

4. Richard F. Dechant and Peter K. Mueller, "Performance of a Continuous NDIR Carbon Monoxide Analyzer," AIHL Report No. 57, Air and Industrial Hygiene Laboratory, Department of Public Health, Berkeley, California, June 1969.

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7. John Mandel, The Statistical Analysis of Experimental Data, Interscience Publishers, Division of John Wiley & Sons, New York, N. Y., 1964.

APPENDIX

REFERENCE METHOD FOR THE CONTINUOUS MEASUREMENT OF CARBON MONOXIDE IN THE ATMOSPHERE (NON-DISPERSIVE INFRARED SPECTROMETRY)

Reproduced from Appendix C, "National Primary and Secondary Ambient Air Quality Standards." *Federal Register,* Vol 36, No. 84, Part II, Friday, April 30, 1971

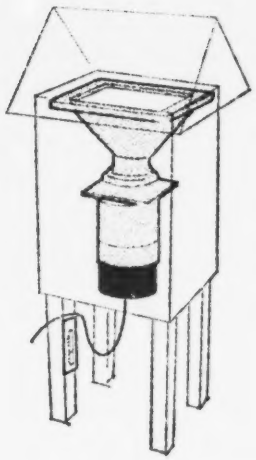

Figure B2. Assembled sampler and shelter.

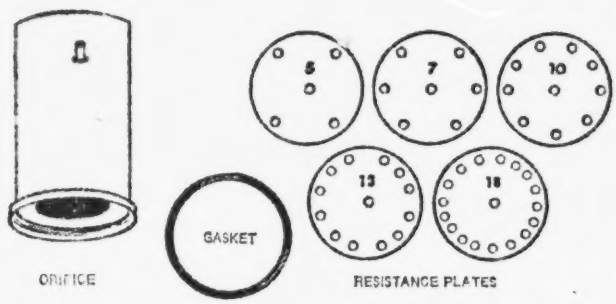

Figure B3. Orifice calibration unit.

APPENDIX C—REFERENCE METHOD FOR THE CONTINUOUS MEASUREMENT OF CARBON MONOXIDE IN THE ATMOSPHERE (NON-DISPERSIVE INFRARED SPECTROMETRY)

1. *Principle and Applicability.*

1.1 This method is based on the absorption of infrared radiation by carbon monoxide. Energy from a source emitting radiation in the infrared region is split into parallel beams and directed through reference and sample cells. Both beams pass into matched cells, each containing a selective detector and CO. The CO in the cells absorb infrared radiation only at its characteristic frequencies and the detector is sensitive to those frequencies. With a nonabsorbing gas in the reference cell, and with no CO in the sample cell, the signals from both detectors are balanced electronically. Any CO introduced into the sample cell will absorb radiation, which reduces the temperature and pressure in the detector cell and displaces a diaphram. This displacement is detected electronically and amplified to provide an output signal.

1.2 This method is applicable to the determination of carbon monoxide in ambient air, and to the analysis of gases under pressure.

2. *Range and Sensitivity.*

2.1 Instruments are available that measure in the range of 0 to 58 mg./m.³ (0–50 p.p.m.), which is the range most commonly used for urban atmospheric sampling. Most instruments measure in additional ranges.

2.2 Sensitivity is 1 percent of full-scale response per 0.6 mg. CO/m.³ (0.5 p.p.m.).

3. *Interferences.*

3.1 Interferences vary between individual instruments. The effect of carbon dioxide interference at normal concentrations is minimal. The primary interference is water vapor, and with no correction may give an interference equivalent to as high as 12 mg. CO/m.³ Water vapor interference can be minimized by (a) passing the air sample through silica gel or similar drying agents, (b) maintaining constant humidity in the sample and calibration gases by refrigeration, (c) saturating the air sample and calibration gases to maintain constant humidity or (d) using narrowband optical filters in combination with some of these measures.

3.2 Hydrocarbons at ambient levels do not ordinarily interfere.

4. *Precision, Accuracy, and Stability.*

4.1 Precision determined with calibration gases is ±0.5 percent full scale in the 0–58 mg./m.³ range.

4.2 Accuracy depends on instrument linearity and the absolute concentrations of the calibration gases. An accuracy of ±1 percent of full scale in the 0–58 mg./m.³ range can be obtained.

4.3 Variations in ambient room temperature can cause changes equivalent to as much as 0.5 mg. CO/m.³ per °C. This effect can be minimized by operating the analyzer in a temperature-controlled room. Pressure changes between span checks will cause changes in instrument response. Zero drift is usually less than ±1 percent of full scale per 24 hours, if cell temperature and pressure are maintained constant.

5. *Apparatus.*

5.1 *Carbon Monoxide Analyzer.* Commercially available instruments should be installed on location and demonstrated, preferably by the manufacturer, to meet or exceed manufacturers specifications and those described in this method.

5.2 *Sample Introduction System.* Pump, flow control valve, and flowmeter.

5.3 *Filter (In-line).* A filter with a porosity of 2 to 10 microns should be used to keep large particles from the sample cell.

5.4 *Moisture Control.* Refrigeration units are available with some commercial instruments for maintaining constant humidity. Drying tubes (with sufficient capacity to operate for 72 hours) containing indicating silica gel can be used. Other techniques that prevent the interference of moisture are satisfactory.

6. *Reagents.*

6.1 *Zero Gas.* Nitrogen or helium containing less than 0.1 mg. CO/m.³

6.2 *Calibration Gases.* Calibration gases corresponding to 10, 20, 40, and 80 percent of full scale are used. Gases must be provided with certification or guaranteed analysis of carbon monoxide content.

6.3 *Span Gas.* The calibration gas corresponding to 80 percent of full scale is used to span the instrument.

7. *Procedure.*

7.1 Calibrate the instrument as described in 8.1. All gases (sample, zero, calibration, and span) must be introduced into the entire analyzer system. Figure C1 shows a typical flow diagram. For specific operating instructions, refer to the manufacturer's manual.

8. *Calibration.*

8.1 *Calibration Curve.* Determine the linearity of the detector response at the operating flow rate and temperature. Prepare a calibration curve and check the curve furnished with the instrument. Introduce zero gas and set the zero control to indicate a recorder reading of zero. Introduce span gas and adjust the span control to indicate the proper value on the recorder scale (e.g. on 0–58 mg./m.³ scale, set the 46 mg./m.³ standard at 80 percent of the recorder chart). Recheck zero and span until adjustments are no longer necessary. Introduce intermediate calibration gases and plot the values obtained. If a smooth curve is not obtained, calibration gases may need replacement.

9. *Calculations.*

9.1 Determine the concentrations directly from the calibration curve. No calculations are necessary.

9.2 Carbon monoxide concentrations in mg./m.³ are converted to p.p.m. as follows:

$$\text{p.p.m. CO} = \text{mg. CO/m.}^3 \times 0.873$$

10. *Bibliography.*

The Intech NDIR–CO Analyzer by Frank McElroy. Presented at the 11th Methods Conference in Air Pollution, University of California, Berkeley, Calif., April 1, 1970.

Jacobs, M. B. et al., J.A.P.C.A. *9, No. 2,* 110–114, August 1959.

MSA LIRA Infrared Gas and Liquid Analyzer Instruction Book, Mine Safety Appliances Co., Pittsburgh, Pa.

Beckman Instruction 1635B, Models 215A, 315A and 415A Infrared Analyzers, Beckman Instrument Company, Fullerton, Calif.

Continuous CO Monitoring System, Model A 5611, Intertech Corp., Princeton, N.J.

Bendix—UNOR Infrared Gas Analyzers, Ronceverte, W. Va.

ADDENDA

A. *Suggested Performance Specifications for NDIR Carbon Monoxide Analyzers:*

Range (minimum)	0–58 mg./m.³ (0–50 p.p.m.).
Output (minimum)	0–10, 100, 1,000, 5,000 mv. full scale.
Minimum detectable sensitivity.	0.6 mg./m.³ (0.5 p.p.m.).
Lag time (maximum)	15 seconds.
Time to 90 percent response (maximum).	30 seconds.
Rise time, 90 percent (maximum).	15 seconds.
Fall time, 90 percent (maximum).	15 seconds.
Zero drift (maximum)	3 percent/week, not to exceed 1 percent/24 hours.
Span drift (maximum)	3 percent/week, not to exceed 1 percent/24 hours.
Precision (minimum)	±0.5 percent.
Operational period (minimum).	3 days.
Noise (maximum)	±0.5 percent.
Interference equivalent (maximum).	1 percent of full scale.
Operating temperature range (minimum).	5–40° C.
Operating humidity range (minimum).	10–100 percent.
Linearity (maximum deviation).	1 percent of full scale.

B. *Suggested Definitions of Performance Specifications:*

Range—The minimum and maximum measurement limits.

Output—Electrical signal which is proportional to the measurement; intended for connection to readout or data processing devices. Usually expressed as millivolts or milliamps full scale at a given impedance.

Full Scale—The maximum measuring limit for a given range.

Minimum Detectable Sensitivity—The smallest amount of input concentration that can be detected as the concentration approaches zero.

Accuracy—The degree of agreement between a measured value and the true value; usually expressed as ± percent of full scale

Lag Time—The time interval from a step change in input concentration at the instrument inlet to the first corresponding change in the instrument output.

Time to 90 percent Response—The time interval from a step change in the input concentration at the instrument inlet to a reading of 90 percent of the ultimate recorded concentration.

Rise Time (90 percent)—The interval between initial response time and time to 90 percent response after a step increase in the inlet concentration.

Fall Time (90 percent)—The interval between initial response time and time to 90 percent response after a step decrease in the inlet concentration.

Zero Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is zero; usually expressed as percent full scale.

Span Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is a stated upscale value; usually expressed as percent full scale.

Precision—The degree of agreement between repeated measurements of the same concentration, expressed as the average deviation of the single results from the mean.

Operational Period—The period of time over which the instrument can be expected to operate unattended within specifications.

Noise—Spontaneous deviations from a mean output not caused by input concentration changes.

Interference—An undesired positive or negative output caused by a substance other than the one being measured.

Interference Equivalent—The portion of indicated input concentration due to the presence of an interferent.

Operating Temperature Range—The range of ambient temperatures over which the instrument will meet all performance specifications.

Operating Humidity Range—The range of ambient relative humidity over which the instrument will meet all performance specifications.

Linearity—The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between upper and lower calibration points.

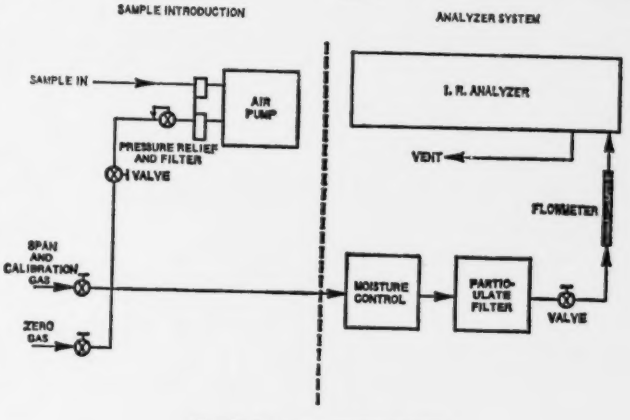

Figure C1. Carbon monoxide analyzer flow diagram.

APPENDIX D—REFERENCE METHOD FOR THE MEASUREMENT OF PHOTOCHEMICAL OXIDANTS CORRECTED FOR INTERFERENCES DUE TO NITROGEN OXIDES AND SULFUR DIOXIDE

1. *Principle and Applicability.*

1.1 Ambient air and ethylene are delivered simultaneously to a mixing zone where the ozone in the air reacts with the ethylene to emit light which is detected by a photomultiplier tube. The resulting photocurrent is amplified and is either read directly or displayed on a recorder.

1.2 The method is applicable to the continuous measurement of ozone in ambient air.

2. *Range and Sensitivity.*

2.1 The range is 9.8 ng. O_3/m.³ to greater than 1960 ng. O_3/m.³ (0.005 p.p.m. O_3 to greater than 1 p.p.m. O_3).

2.2 The sensitivity is 9.8 ng. O_3/m.³ (0.005 p.p.m. O_3).

3. *Interferences.*

3.1 Other oxidizing and reducing species normally found in ambient air do not interfere.

4. *Precision and Accuracy.*

4.1 The average deviation from the mean of repeated single measurements does not exceed 5 percent of the mean of the measurements.

4.2 The method is accurate within ±7 percent.

5. *Apparatus.*

5.1 *Detector Cell.* Figure D1 is a drawing of a typical detector cell showing flow paths of gases, the mixing zone, and placement of the photomultiplier tube. Other flow paths in which the air and ethylene streams meet

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